

**STARCH CROSSLINKING FOR CELLULOSE FIBER
MODIFICATION AND STARCH NANOPARTICLE FORMATION**

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by

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**STARCH CROSSLINKING FOR CELLULOSE FIBER
MODIFICATION AND STARCH NANOPARTICLE FORMATION**

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In memory of my father, Junpeng Song

**Dedicated to my mother, Huaxiang Liu,
and my wife, Na Zhang**

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SUMMARY

As a low cost natural polymer, starch is widely used in paper, food, adhesive, and many other industries. In order to improve the performance of starch, crosslinking is often conducted either in the processes of starch modification or during the application processes. For example, by controlling the degree of crosslinking, the water retention value of starch-based hydrogel can be well controlled. In addition, the adhesive and bonding strength of starch on a substrate can be significantly improved by controlling the degree of starch crosslinking. Many crosslinkers have been developed in the past for crosslinking starch. Ammonium zirconium carbonate (AZC) is one of the common crosslinkers for crosslinking starch in aqueous solutions, having been widely used as a starch crosslinking agent in paper surface coating for more than 20 years. However, the mechanisms of starch crosslinking with AZC have not been well studied. In order to optimize the crosslinking chemistry of starch and find new paths for the utilization of starch in papermaking, a better understanding of the starch crosslinking mechanism is necessary.

This thesis focuses on the fundamental study of starch crosslinking in an aqueous solution and its applications in fiber surface grafting, filler modification, and starch nanoparticle formation. Particularly, the thesis contains three major parts:

(1) Mechanism study of starch crosslinking induced by AZC

The possible reaction mechanism between AZC and starch has been proposed in the literature. However, the kinetics of starch crosslinking by AZC and the physical

properties of crosslinked starch-AZC network have not been studied. In this thesis, the crosslinking (or gelation) kinetics of starch/AZC blends were investigated by using rheological measurements. The evolution of viscoelastic properties of AZC solutions and the AZC-starch blends was characterized. It was found that for both AZC self-crosslinking and AZC-starch co-crosslinking, the initial bond formation rate and the gel strength had a strong power law relationship with the concentrations of both AZC and starch. It is suggested that the development of the crosslinking network is highly dependent on the AZC concentration, while the starch concentration effect is less significant. It was determined that the activation energy of AZC self-crosslinking was approximately 145-151 kJ/mol, while the activation energy of AZC-starch co-crosslinking was 139 kJ/mol.

(2) Fiber and filler modifications with starch and crosslinkers

Besides reacting with starch, AZC can react with cellulose which also contains hydroxyl groups. Theoretically, it is possible to use AZC as a crosslinker / coupling agent to graft starch onto cellulose fibers. It is believed that the grafted starch on fiber surfaces can improve the fiber bonding capability. In this thesis, a facile method to graft starch onto cellulose fiber surfaces through the hydrogen bond formation among cellulose, starch and AZC was developed. Compared with the paper sheets made of fibers with an industry refining level (420 ml CSF), the paper sheets made of fibers with a much lower refining degree but with grafted starch showed higher paper strengths, including the tensile strength, stiffness and z direction tensile; meanwhile, a faster drainage rate during web formation could also be achieved.

Not only can the fiber-fiber bonding be improved by grafting starch onto fiber surfaces, but the filler-fiber bonding can also be improved if starch can be effectively coated on the filler surface. This concept has been supported by the early studies. In this thesis, the effects of the crosslinking of starch in the filler modification for the papermaking application were also studied.

(3) Mechanism of starch nanoparticle formation during extrusion with crosslinkers

It was reported that starch crosslinking could facilitate the reduction of starch particle size during reactive extrusion. However, the mechanism of the particle size reduction by starch crosslinking was not illustrated. The reason that the crosslinking can cause the particle size reduction of starch during extrusion is fundamentally interesting. In this thesis, the mechanism of starch particle size reduction during extrusion with and without crosslinkers was investigated by identifying the contributions of thermal and mechanical effects. The effects of extrusion conditions, including temperature, screw speed, torque, starch water content and crosslinker addition, on the particle size were studied. It was found that the addition of crosslinkers could significantly increase the shear force (torque), and consequently facilitate the reduction of the particle size. The results indicate that for extrusion without a crosslinker, the starch particle size decreased with the increase of temperature. At 100°C, the starch particles with a size of 300 nm could be obtained. With the addition of appropriate crosslinkers (glyoxal), the starch particle size could be reduced to around 160 nm, even at a lower extrusion temperature of 75°C.

CHAPTER 1

INTRODUCTION

Starch is widely used in food and other industrial applications, such as papermaking and adhesives. In paper coating, starch is a commonly used binder. In order to improve the performance of the binder, a crosslinker/insolubilizer, ammonium zirconium carbonate (AZC) is normally used to crosslink starch molecules in the coating film. The possible reaction mechanism between AZC and starch has been proposed in the literature, and the effect of AZC addition on coating rheology has been investigated by researchers (McAlpine 1982; McAlpine 1985; Moles 1987; Wolff, Calcar et al. 1996; Ryu, Gilbert et al. 1999; Scholz, kamutzki et al. 2007). However, the kinetics of the starch crosslinking by AZC and the properties of the crosslinked starch network have not been thoroughly studied. In order to optimize the use of starches and/or crosslinkers in current applications and to find some new applications, a better understanding of the above aspects of starch crosslinking process is necessary.

In papermaking and paper coating, starches must be well cooked before use. However, cooked starches have many drawbacks, including a high viscosity and a limited absorption amount on cellulose substrates, which might cause operational problems or poor starch performance. It was reported that nano-sized starch had superior properties, including a low viscosity at high concentrations and higher bonding capability (Bloembergen, McLennan et al. 2008). A high yield, environmentally friendly method for preparing starch nanoparticles via reactive extrusion was proposed in a patent (Giezen,

Jongboom et al. 2000). However, the mechanism of starch particle size reduction, particularly the effect of starch crosslinking during extrusion has not been well understood. With an adequate understanding of the mechanism of starch particle reduction during extrusion, the extruded starch particle size can be tailored according to the different purposes of the final uses.

This dissertation focused mainly on the fundamental understanding of starch crosslinking in the above two issues. As new applications of starch in papermaking, fiber and filler modifications with starch and crosslinkers were also studied.

Chapter 2 introduces some background information about starch chemistry, starch crosslinking and starch applications in papermaking. The previous researches in fiber modification, filler modification and starch nanoparticle preparation are also reviewed. **Chapter 3** outlines the objectives of this thesis research, including both fundamental understandings and new applications of starch crosslinking. **Chapter 4** provides an exploration of the kinetics of AZC self-crosslinking and the co-crosslinking of starch-AZC. The effects of AZC concentration, starch concentration, temperature and pH values on the crosslinking process are discussed. **Chapter 5** develops a new method of fiber modification via starch grafting by using AZC as a crosslinking/coupling agent. **Chapter 6** presents the effects of the starch grafting treatment on water drainage, water removal in the wet web press and drying section, and paper properties. The study on repulping of dry pulp board made of starch grafted fibers is also discussed. **Chapter 7** demonstrates one problem related to starch-coated filler, i.e. the breaking up of starch-coated fillers in

water. The significant improvement of the rewetting stability of the starch-coated filler caused by a crosslinker addition in the process of filler modification and the effect of starch crosslinking on paper tensile strength are further presented. **Chapter 8** describes the mechanism of starch nanoparticle formation during extrusion. Also discussed are the effects of extrusion conditions, including temperature, screw speed, torque, starch water content and a crosslinker addition, on the particle size. **Chapter 9** summarizes the conclusions for the thesis and provides recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to starch

2.1.1 Origin of starch

Starch is the second most abundant natural polymer on Earth. As an energy reserve in various plants, starch exists in seeds, stalks, and roots of staple crops such as potato, corn, rice, wheat, and tapioca (Le Corre, Bras et al. 2010). In plants, glucose is first produced via photosynthesis, and then stored in the form of starch granules. The size and shape of starch granules vary for different biological sources (Table 2.1).

Table 2.1 Size and shape of starch granules in different plants (Jane, Shen et al. 1992; Buléon, Colonna et al. 1998; Lindeboom, Chang et al. 2004; Tester, Karkalas et al. 2004; Ayoub & Rizvi 2009)

Plant sources	size (µm)	shape
potato	5-100	oval
maize	2-30	round and polyhedral
maize waxy	2-30	round and polyhedral
wheat	<10 & 10-35	discs
rice	2-10	polyhedral
tapioca	5-45	spherical / lenticular

2.1.2 Chemistry of starch

Chemically, starch is a glucose polymer made with glucopyranose units bonded in α -linkages. As a polysaccharide, starch has two forms in nature: amylose and amylopectin (Tester, Karkalas et al. 2004). Amylose is a linear chain polymer with several hundred glucose units in α (1 \rightarrow 4) linkages (Figure 2.1 left). The molecular weight of amylose is around 10^5 - 10^6 g/mol (Wesslén & Wesslén 2002). However, amylopectin is a highly branched molecule with several thousand glucose units (Figure 2.1 right). In amylopectin molecules, α (1 \rightarrow 4) glucan chains are interlinked by α (1 \rightarrow 6) linkages, resulting in a branched structure (Buléon, Colonna et al. 1998). The molecular weight of amylopectin is within the range of 10^7 to 10^9 g/mol (Buléon, Colonna et al. 1998). Normally, there are 15-30% amylose and 70-85% amylopectin in starch, depending on the species of source. As a special specie, waxy maize only contains less than 1% amylose (Buléon, Colonna et al. 1998).

Amylose can complex with different hydrophobic ligands, including iodine, potassium hydroxide, potassium bromide, aroma compound, dimethyl sulfoxide (DMSO), lipids and linear alcohols (Kim & Lim 2009). The resultant complexes are called V type amyloses.

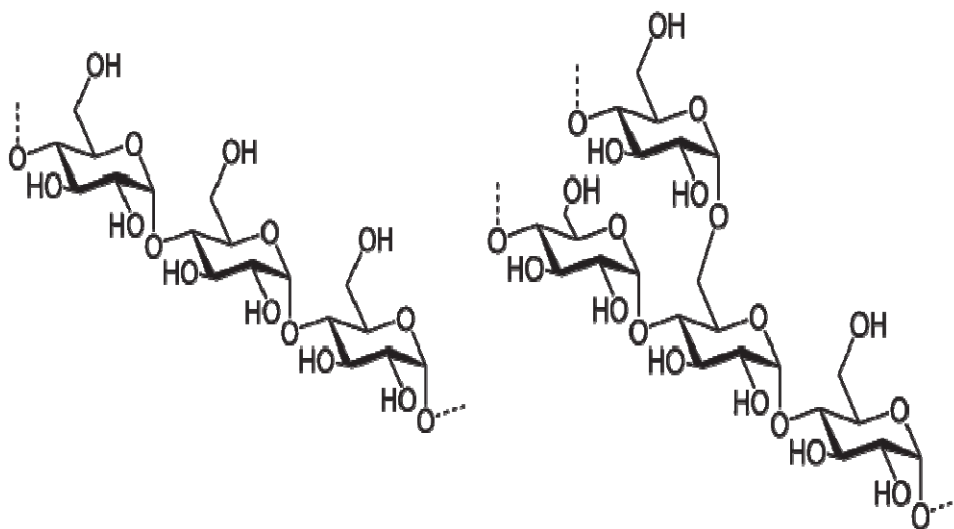


Figure 2.1 Molecular structures of starch (left: amylose; right: amylopectin).

2.1.3 Crystal structure of starch

Native starch granules consist of alternating amorphous and semi-crystalline growth rings which form an onion-like structure (Angellier, Putaux et al. 2005). It was reported that starch granules showed a lamellar structure which consists of stacks of nanometric subunits with a periodicity of 9-10 nm (Figure 2.2) (Donald, Waigh et al. 1997; Putaux, Molina-Boisseau et al. 2003; Tester, Karkalas et al. 2004). In starch granules, it is believed that amylose exists in the amorphous noncrystalline region of starch, and a clustered organization of amylopectin side chains forms the crystalline regions (Putaux, Molina-Boisseau et al. 2003; Blanche & Sun 2004).

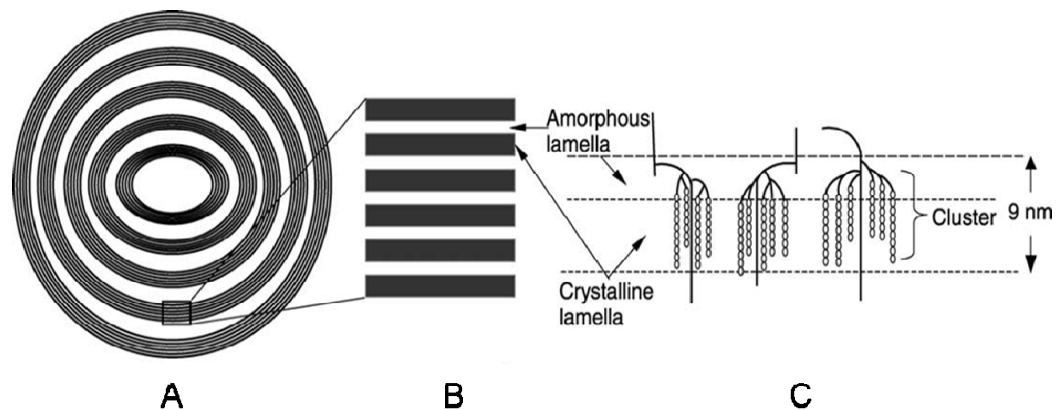


Figure 2.2 A schematic representation of the lamellar structure of a starch granule (Donald, Waigh et al. 1997). (A. Alternating amorphous growth rings and stacks of microcrystalline lamellae. B. Magnified view of the crystalline lamellae and amorphous lamellae. C. Crystalline lamellae consist of double helical structures formed by adjacent chains of amylopectin. The amorphous regions are formed by branching points.)

The crystal structure of native starch granules can be determined by x-ray diffraction diagrams (Figure 2.3). Cereal starches, such as maize, exhibit an A type crystal, while tuber and amylose rich starches normally show a B type crystal (Buléon, Colonna et al. 1998). C type crystal would be shown when A and B crystals are coexisting in starch. During the gelatinization of starch, the V type crystalline x-ray pattern is demonstrated, referring to the complex of amylose with fatty acids and monoglycerides.

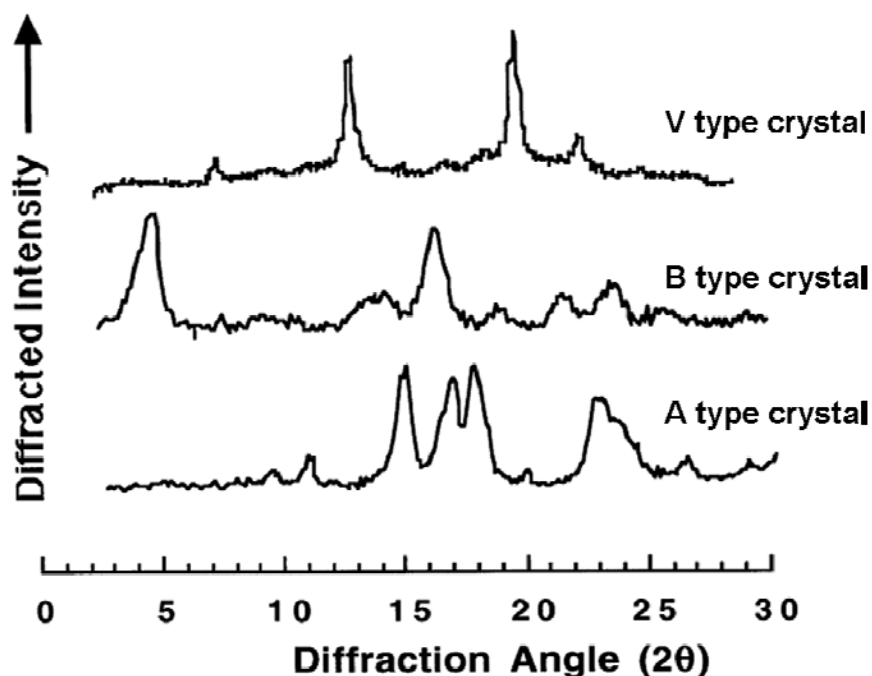


Figure 2.3 X-ray diffraction diagrams of different types of starch (Buléon, Colonna et al. 1998).

The degree of crystallinity refers to the percentage of the crystalline regions with respect to the total materials. By analyzing x-ray diffraction pattern, the crystallinity of starch can be determined via two different techniques. Based on the two-phase concept, *i.e.* the diffraction pattern can be separated into crystal and amorphous parts, Sterling (Sterling 1960) and Nara (Nara, Mori et al. 1978) first proposed a technique to calculate starch crystallinity. In this technique, the areas corresponding to the contribution of amorphous and crystalline region are determined and compared, and then the crystallinity can be determined. However, according to the crystal-defect concept, the simple pattern separation method is questionable because a portion of x-ray scattering from the crystalline region can diffuse and cause the change of the amorphous background. The second technique for determining starch crystallinity is to compare the experimental diagrams to several discrete crystalline diffraction peaks (100% crystallinity diagrams)

and an amorphous halo (100% amorphous diagram) (Buléon, Colonna et al. 1998; Lopez-Rubio, Flanagan et al. 2008). Although different results based on different techniques were reported, a typical range of the crystallinity of starch granules is around 15-45% (Zobel 1988).

X-ray powder diffraction is only sensitive to some information at the long range order, such as the crystal structure and the relative crystallinity of starch. For the short range order, Nuclear magnetic resonance (NMR) can be used to determine the fine structures, such as the local molecular structure and the conformational order. Cheetham and Tao studied the structure and conformational properties of maize starch by utilizing solid state NMR (Cheetham & Tao 1998a). The chemical shifts, relative resonance intensities, line-widths and spectral shapes were analyzed for different starch samples.

2.1.4 Gelatinization and retrogradation of starch

Native starch granules are insoluble in cold water. However, when the starch slurry is heated to a certain temperature range (the gelatinization temperature), the granules swell rapidly by absorbing water. The absorbed water enters the amorphous regions of the granules. The intermolecular hydrogen bonds holding the granules together are disassociated. After the granules swell to many times their original volume, the granular units are disrupted and collapse with continued heating and agitation. After the starch granules are completely fragmented, a starch solution is produced (Jonhed 2006). Different starches have different gelatinization temperatures at a range of 55 to 80°C.

The gelatinization process of starches can be monitored by a differential scanning calorimeter (DSC) measurement (Yu & Christie 2001).

For some applications, starch pastes or solutions need to be prepared by following a certain cooking process. During the cooking process, starch slurries would experience a viscosity increase step, followed by a viscosity decrease step. The viscosity change of starch dispersion during cooking is normally monitored and characterized by using a Brabender viscograph (Figure 2.4).

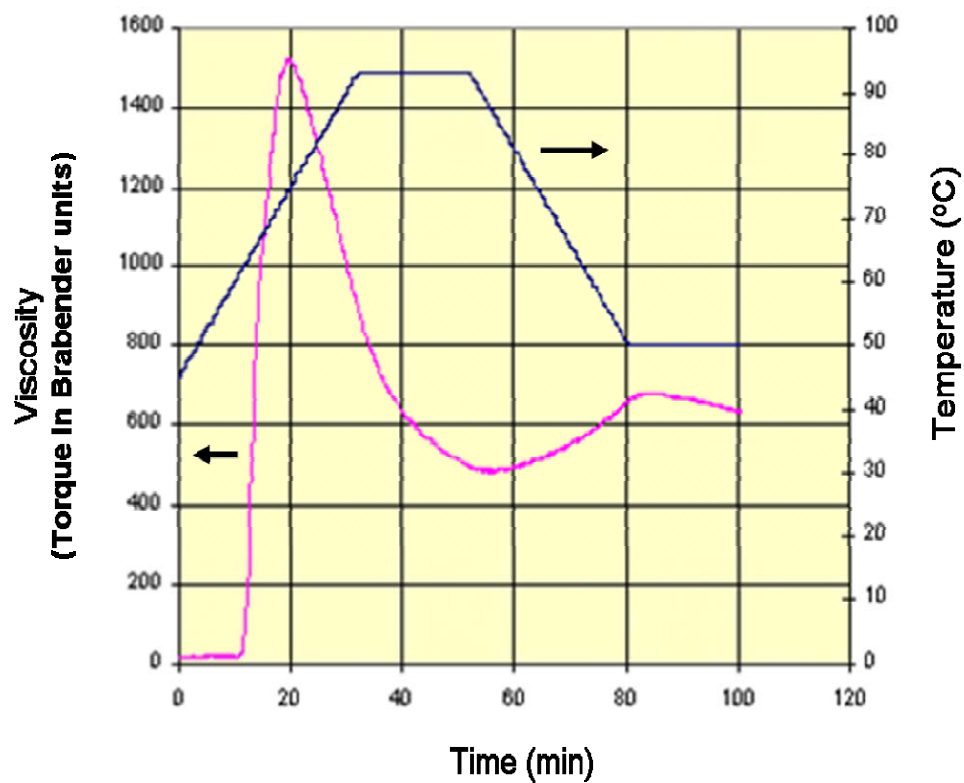


Figure 2.4 A typical Brabender viscograph of starch (www.starch.dk/isi/starch/potato.asp)

When cooked starch solutions are cooled, hydrogen bonds are formed between the hydrated amylose molecules, and the chains wrap around to form double helices, resulting in the formation of colloidal crystallites. This phenomenon is called retrogradation which is a non-reversible process (Imberty, Buléon et al. 1991). Many factors, such as starch concentration, molecular weight, degree of hydration, temperature, pH and salt concentration, may affect the rate of retrogradation. For diluted starch solutions, particulate precipitation can be observed. For solutions with high concentrations, a gel is normally formed (Jonhed 2006).

2.1.5 Starch applications

As an abundant natural polymer, starch has many attractive properties, such as biodegradability, biocompatibility, and low cost. Since starch is a low-cost versatile biopolymer, it has been widely used in food and non-food applications (Jobling 2004; Ayoub & Rizvi 2009; Song, Zhao et al. 2009). It is reported that about 55% of total starch production is used in food applications, while 45% is for non-food applications (Myllarinen 2002). Starch is a natural food ingredient in human diet. In the food industry, starches can be used for thickening, emulsion stabilization, flowing aid, encapsulation, molding, gelling and so forth (Light 1989). As a biodegradable natural polymer with nontoxicity and a good chemical reactivity, starch is also widely used in non-food applications, including adhesives, fermentation, additives for papermaking, coating, additives for plastics, cosmetics and pharmaceutical products (Kim & Lee 2002; Ayoub

& Rizvi 2009). For example, in pharmaceutical industry, starch can be used as fillers and carrier materials.

2.2 Starch modification

Starch is a low cost abundant natural polymer. However, native starches normally have hydrophilic property, high viscosity of paste, and low resistance to acids. Therefore, the native starches have limited use. In order to induce or enhance some special properties, native starches normally need to be modified mechanically, chemically or enzymatically. The common purposes of starch modifications are to change pasting temperatures, reduce viscosity of pastes, improve resistance to processing conditions (acids, heat, mechanical shear), and add desirable function groups (Ayoub & Rizvi 2009).

2.2.1 Physical modification of starch

Pregelatinization, particle size reduction and moisture adjustments are typical physical modifications on starches (Light 1989). For some specific applications, such as fat substitutes and filler in plastic films, a smaller granule size is required (Jane, Shen et al. 1992). Ball mill grinding, high pressure homogenization, and extrusion are typical means used for reducing starch particle sizes. The preparation of starch nanoparticles via reactive extrusion will be discussed in detail in later sections.

2.2.2 Chemical modification of starch

In each glucose unit of amylose molecules, there are 2 secondary hydroxyl groups (at C-2 and C-3) and one primary hydroxyl group at C-6 (Tomasik & Schilling 2004). In amylopectin molecules, each branch substitutes one primary (at C-6) hydroxyl group, but at the same time, one secondary hydroxyl group (at C-4) is introduced. Therefore, besides the two hydroxyl groups on the ends, in each glucose residue of amylopectin, there are still three hydroxyl groups either as primary groups or secondary groups. All these available hydroxyl groups have potentials of reactivity to form hydrogen bonds, to be oxidized and reduced, to form esters and ethers, or to be substituted by other functional groups (Tomasik & Schilling 2004). The three available free hydroxyl groups have different reactivities. The primary hydroxyl group at C-6 is more reactive than the two secondary hydroxyl groups which have a steric hindrance. As the hydroxyl group at C-2 is closer to the hemi-acetal and more acidic than the hydroxyl group at C-3, it is more reactive than the hydroxyl group at C-3 (Xu, Miladinov et al. 2004). The objective of chemical modifications of starches is to introduce some changes on these hydroxyl groups.

The methods of chemical modifications of starches normally include acid hydrolysis, oxidation, substitution, and crosslinking. Chemical modifications of starches are normally conducted under dilute conditions (aqueous slurry or solution) or under semi-dry conditions (extrusion) (Gotlieb & Capelle 2005). Reactive extrusion is a common process for starch modifications (Xie, Yu et al. 2006). In the reactor (extruder), various

chemicals, such as acid, alkalis, enzymes, crosslinkers, can be added to react with starches for different purposes. Many modified starches, such as carboxymethylated starches, starch phosphates, starch-fatty acid esters, cationic starches and anionic starches have been prepared via an extrusion method (Valle, Colonna et al. 1991; Miladinov & Hanna 2000). Xie et al. gave a brief review of applications of reactive extruders for starch modifications (Xie, Yu et al. 2006).

Acid modification of starch

Acid modifications can change the structure and physicochemical properties of starches, such as molar mass, crystallinity, viscosity, gelatinization temperature, and gel rigidity (Hoover 2000; Beninca, Demiate et al. 2008). Typically, native starch granules are treated with mineral acids (such as hydrochloric acid and sulfuric acid) for an extended time at a temperature below the gelatinization temperature of starches (Wang, Truong et al. 2003). During the treatment, the hydroxonium ions attack the glycosidic oxygen atoms, resulting in the scission of the glucosidic linkages. The amorphous regions can be dissolved/hydrolyzed, and consequentially the separation and release of crystalline sections can be realized by vigorous mechanical shearing (Kristo & Biliaderis 2007; Dufresne 2008). Therefore, the acid hydrolyzed starches normally have higher degrees of crystallinity, compared to original starches.

After treatment, aqueous suspensions of nanocrystals (platelets) are normally obtained. With an acid treatment, the solubility and the gel strength of starches can be increased,

and the viscosity can be decreased (Kim & Ahn 1996). For example, thin boiling starches and soluble starches can be prepared via aid treatments for specific applications. The resultant nanocrystals can be used for implant materials, drug carriers, and reinforcing elements for composites (Thielemans, Belgacem et al. 2006).

Oxidation of starch

For some applications, such as high shear coatings, a low viscosity of starch solutions is required. For this purpose, the molecular weight of native starches has to be reduced via oxidation. By using some oxidation agents, such as sodium hypochlorite, the hydroxyl groups on starch molecules are first oxidized to carbonyl groups, and then finally to carboxyl groups. The level of oxidation, or degree of substitution (DS) depends on the average number of carboxyl and carbonyl groups introduced per glucose unit. For the oxidized solutions, the associative tendencies of starch molecules are hindered due to the sterical effect of introduced carboxyl and carbonyl groups (Jonhed 2006). Therefore, compared to native starches, oxidized starches have a much lower viscosity, and higher slurry stability even at a high concentration, which makes it useful for many industry applications without runnability problems.

Substitution of starch

As mentioned early, on each anyhydroglucose unit of starch molucules there are three hydroxyl groups which may be substituted. The average number of substitutions per

anhydroglucose unit in starches is defined as the degree of substitution (DS). Therefore, the highest DS value is 3. The hydroxyl groups on starch are partially substituted with some ionic groups, producing starch esters, starch ethers, anionic starches, cationic starches. Small amount of ionic or hydrophobic groups can be introduced into the starch molecules to change the properties of starches (Wesslén & Wesslén 2002). For example, cationic starches can be prepared by introducing cationic substituent groups to the hydroxyl group of starch molecules via ether linkages. Tertiary amino derivatives and quaternary amino derivatives are two typical cationic starches used in the paper industry. Starch acetates can be prepared by substituting the free hydroxyl groups with acetyl groups. Starch acetates with a low DS (0.01-0.2) are allowed to be used in food, while the starch acetates with high DS can be applied as a replacement for cellulose acetates (Xu, Miladinov et al. 2004). As the hydrophobicity of starches is increased with the DS, the starch acetates with a higher DS have a higher miscibility with hydrophobic plastic polymers. Normally, after substitution modifications, the granular form of starches can be maintained.

Crosslinking of starch

Crosslinking occurs when bonding bridges are introduced between adjacent molecules (Kling 2001). In order to crosslink polymers containing hydroxyl groups on the backbones, such as starches, the crosslinkers must have a capability to react with at least two hydroxyl groups in a single polymer molecule or in adjacent molecules (Steiger 1966). For starch crosslinking, bifunctional and multifunctional reagents are normally

used to form ether, ester or other linkages with the hydroxyl groups in starch molecules (Ayoub & Rizvi 2009). Sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin, and phosphoryl chloride, are normally used crosslinkers (Silva, Ibezim et al. 2006; Ayoub & Rizvi 2009). Starch crosslinking can be accomplished via either covalent crosslinking or noncovalent interactions. The noncovalent crosslinking, such as hydrogen bonding, is very flexible and reversible in some cases to obtain a controllable polymer network. By varying crosslinker dosages, starch concentration, pH, and temperatures, the extent of crosslinking could be controlled (Ayoub & Rizvi 2009).

The crosslinking treatment of starches can be conducted either in state of granule or in paste state. The reaction conditions vary depending on the crosslinkers used. The reactions are normally performed under neutral to alkaline conditions. However, when aldehydes are used in some cases, the crosslinking should be conducted under acidic conditions (Ayoub & Rizvi 2009). In addition, the crosslinking of starch can also be achieved by irradiation without any additives, which is normally used in grafting processes (Ayoub & Rizvi 2009).

Compared to native starches, crosslinked starches have superior properties in aspects of mechanical, thermal and chemical resistance, such as an improved viscosity, better textural properties, and a higher resistance to high temperature, low pH, and high shear force (Kim & Lee 2002; Nair, Breedveld et al. 2008; Ayoub & Rizvi 2009). Therefore, crosslinked starch hydrogels have many applications, in food, oilfield, pharmaceutical and other industries (Omari 1994).

2.3 Starch crosslinkers for the paper industry

Starch is a typical binder in paper coating formulas, and the use of starch crosslinker in coating is a long time practice. The purposes of using a crosslinker in coating are to insolubilize and immobilize the coating, and to improve the efficiency of binders, i.e. all coating ingredients should be bound together in an “immobile” condition (Wolff 1990). Basically, there are three types of crosslinkers for starches in coating: amino resins, glyoxal, and inorganic crosslinkers (Scholz, kamutzki et al. 2007).

Melamine formaldehyde (MF) and urea formaldehyde (UF) are two typical amino resins for starch crosslinking in paper coating. These two amino resins can react with hydroxyl groups in an acidic solution environment. However, due to the containing of formaldehydes, nowadays amino resins are not commonly used in paper coating as glyoxal and inorganic crosslinkers.

As a dialdehyde compound, glyoxal has been used as a crosslinker for celluloses, starches, and chitosans (Yang, Dou et al. 2005). Glyoxal has two carbonyl groups on its molecules (Figure 2.5 left), and has a strong affinity to hydroxyl groups in starch molecules. Acetalization reaction can occur, i.e. acetal bonds are formed between the hydroxyl groups and aldehydes (Figure 2.5 right). However, glyoxal based resins can not be used for alkaline papermaking because they require an acidic solution environment to achieve crosslinking effects. Heat is also required to initiate reactions and achieve curing.

In addition, as glyoxals still contains formaldehydes, only a limited amount of glyoxal (<6% of starch) is allowed to be used according to the FDA regulation (Wolff 1990).

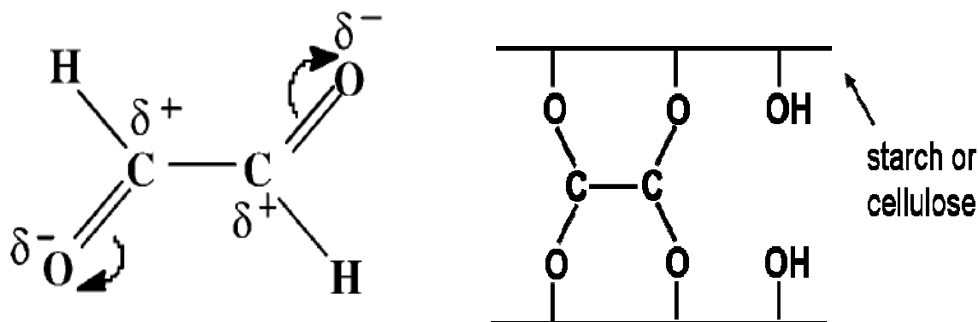


Figure 2.5 Chemical structure of glyoxal (left) and the crosslinked network (right) (Yang, Dou et al. 2005).

Inorganic crosslinkers, such as zirconium compounds can introduce crosslinking via forming chemical bonds, hydrogen bonds, or complexes with reactive groups on polymers.

2.3.1 Chemistry of zirconium compounds

The chemistry and application of zirconium compounds have been intensively investigated. Clearfield (Clearfield 1964) provided a good review on zirconium chemistry, and developed some structural principles based on experimental data. Farnworth and coworkers (Farnworth, Jones et al. 1981) discussed the properties and uses of zirconium chemicals.

A typical and widely used zirconium compound is Ammonium Zirconium Carbonate (AZC). AZC is a soluble alkaline salt, and its aqueous solution is clear and colorless.

Normally, a commercial AZC solution contains 5% ammonium hydroxyl and 20-30% active content (calculated as ZrO_2). Phillips and Holme (Phillips 1977) filed a patent for preparing AZC. AZC solutions contain anionic zirconium compounds, and the zirconium atoms are bridged by hydroxyl groups and bonded with carbonate groups (Figure 2.6). Although it is accepted that AZC can form such polymer chains in aqueous solutions, the degrees of polymerization is hard to be measured due to the sensitivity of the species to their environment (Comyn 1994). Under heating, dilution or pH changes, the decomposition of AZC may occur with the release of ammonia and carbon dioxide. An insoluble gelatinous amorphous solid, carbonated hydrous zirconia, is generated during drying.

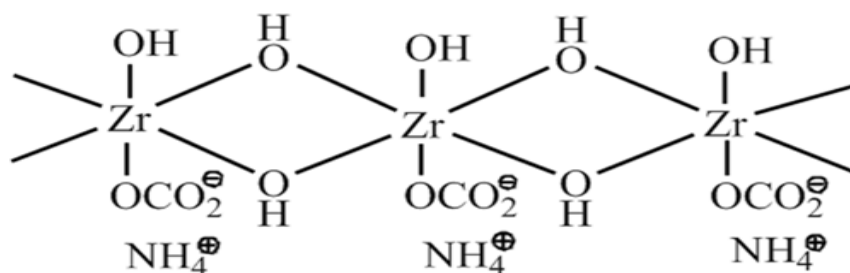


Figure 2.6 Chemical structure of AZC.

Due to a high affinity of zirconium for oxygenated species, AZC can react with hydroxyl groups on organic polymers (McAlpine & Moles 1982). Farnworth (Farnworth, Jones et al. 1981) proposed a possible mechanism of the reaction between AZC and starches: the ammonium ions in AZC solutions can interact with starches via hydrogen bonding to form a pseudo cationic starch, which can link with basic zirconium carbonate ions via ionic attractions (Figure 2.7 a). During drying, ammonia and carbon dioxide are released,

and then new hydrogen bonds are formed between the hydroxyl groups of starches and the reactive sites of AZC (Figure 2.7 b). Similarly, AZC can also react with celluloses by forming hydrogen bonds. According to the above reaction mechanism, the cross-linking reaction can also occur between AZC molecules.

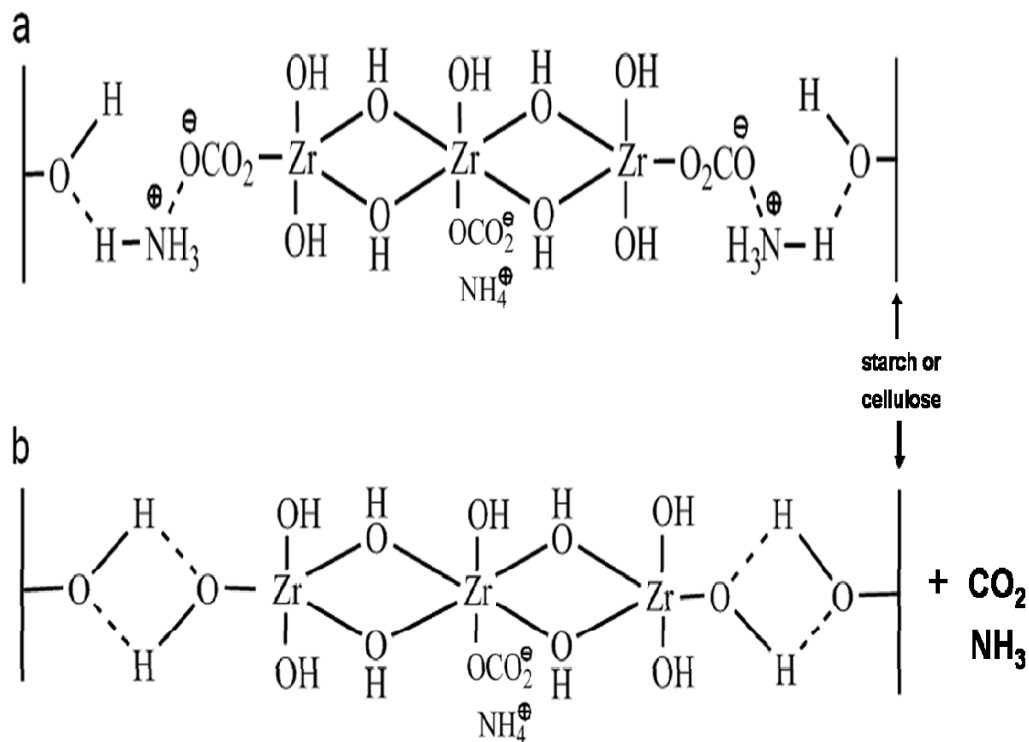


Figure 2.7 The reaction of AZC with polymers containing hydroxyl groups.

So far no direct evidence about the formation of hydrogen bonds between AZC and the polymers containing hydroxyl groups has been reported in the literature. Floyd and Boss (Floyd & Boss 1995) suggested that the increase of starch viscosities under a low shear rate is indirect evidence for the hydrogen bonding interaction. Comyn (Comyn, Dun Han et al. 1993; Comyn 1994) found that the interaction between zirconium propionate and nitrocellulose is moderately strong. He argued that the polymer would be crosslinked and form a strong gel if the interaction were strong enough to form covalent bonds.

2.3.2 Applications of zirconium compounds in papermaking

Because of the low cost, and nontoxic characteristics, there is a long time practice of using zirconium chemicals in the paper industry. Wolff and coworkers (Wolff, Calcar et al. 1996) published a thorough review on the role of AZC in papermaking. Zirconium complexes, such as AZC, are commonly used as insolubilizers or crosslinkers for paper coating (McAlpine 1982; McAlpine 1985; Moles 1987; Moles 1996; Ryu, Gilbert et al. 1999; Aksoy, Joyce et al. 2003; Sherbiny 2004; Whilte 2006; Scholz, kamutzki et al. 2007) and surface sizing formulations (Pandian 1995). Ryu et al. (Ryu, Gilbert et al. 1999) found that AZC could increase the viscosity, yield stress and elastic modulus of coating formulations containing a binder of PVOH. Aksoy and coworkers (Aksoy, Joyce et al. 2003) investigated the effect of AZC on rheological properties of silica/PVOH inkjet coatings. They found that the interaction between zirconium salts and coatings was weak, and decreased with the increase of shear rates. McAlpine (McAlpine 1982; McAlpine 1985) discussed the role of AZC in paper and board coating. He suggested that AZC should be considered as a hydrophilic crosslinker instead of insolubiliser, because AZC could not only impart water resistance but also modify coating structures. Pandian (Pandian 1995) suggested that zirconium salts could form complexes and crosslink both surface sizing polymers (such as starch and carboxymethyl cellulose) and the celluloses on surfaces of sheets, resulting in an improved surface sizing efficiency. Furthermore, Stewart and Wolstenholme (Stewart & Alan 1975) found that the physical properties of paper or woven cotton could be improved by the treatment of zirconium compounds.

Zirconium complexes could also be used to control “stickies” during paper repulping (Brewis, Comyn et al. 1988).

2.3.3 Advantages of AZC over other crosslinkers

Compared to other crosslinkers, such as glyoxal and amine resins, AZC has many advantages. Firstly, AZC can be used under alkaline papermaking condition due to its high pH active range, up to 12. In such conditions, CaCO_3 fillers can be utilized. In contrast, amino resins (melamine formaldehyde resin and urea formaldehyde resin) and glyoxal based resins can not be used for alkaline papermaking because they require an acidic solution environment to achieve crosslinking effects. Both precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) fillers therefore can not be utilized (Pandian 1995) in such conditions. Secondly, for AZC crosslinking, a high temperature is not required to curing, though heat can speed the curing process. Therefore, AZC can be used directly in a water solution to crosslink starch and fibers. In addition, unlike aldehyde and other organic crosslinkers, AZC is not considered as a toxic chemical, and the FDA has approved use of AZC in paper and board products for packaging food (Moles 1996).

2.4 Rheological study on hydrogels

2.4.1 Introduction to rheology

Viscous liquids obey the Newton's law, *i.e.* the shear strain rate is proportional to the stress. The coefficient of proportionality is defined as viscosity (Malkin & Isayev 2005):

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (2.1)$$

where σ is the shear stress, $\dot{\gamma}$ is the shear rate.

For ideal (Newtonian) fluids, such as water, the viscosity is independent of the shear rate (Fig 2.8). If the viscosity decreases with the increase of shear rates, the fluid is shear-thinning (pseudoplastic). If the viscosity increases with the increase of shear rates, the fluid is shear-thickening (dilatancy).

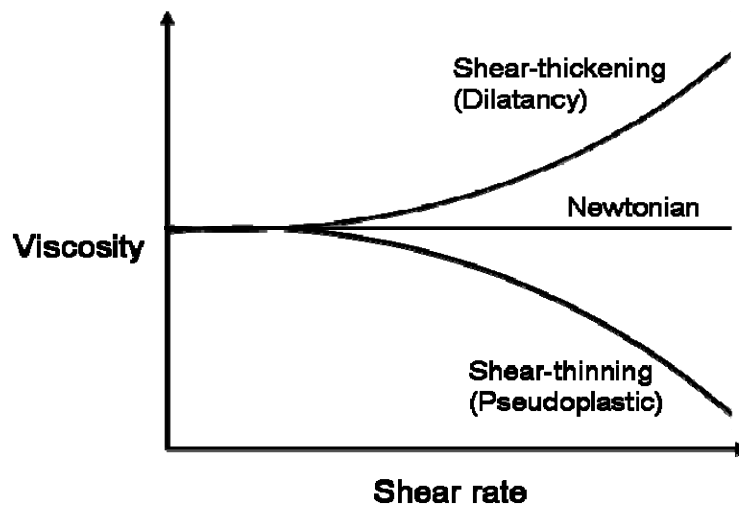


Figure 2.8 Newtonian, shear-thickening and shear-thinning viscosity behaviors.

Elastic materials, or solids, obey the Hooke's law, *i.e.* the stress is proportional to the deformation. The ratio of stress to deformation is called Young's modulus.

However, for many real materials, such as paints, yogurt, toothpastes and grease, they present both liquid-like and solid-like properties (Malkin & Isayev 2005). These materials are called viscoelastic materials, or complex fluids. The semi-dilute or concentrated polymer solutions normally show viscoelastic properties. For viscoelastic materials, their mechanical behaviors cannot be described with the classical disciplines of elasticity and (Newtonian) fluid mechanics. Therefore, a new discipline, rheology was developed as an extension of the classical theories. A traditional definition of rheology is “the study of the flow and deformation of materials” (Malkin & Isayev 2005).

For viscoelastic materials, oscillatory measurements are normally performed to characterize the equilibrium mechanical properties of samples. In oscillatory measurements, the sample is deformed sinusoidally, and a sinusoidal oscillation of stress is generated at the same frequency but with a shift of phase angle δ (Macosko 1994).

$$\gamma = \gamma_o \sin(\omega t) \quad (2.2)$$

$$\tau = \tau_o \sin(\omega t + \delta) \quad (2.3)$$

The ratio of the shear stress to the shear strain, i.e. the complex shear modulus G^* , is expressed as:

$$G^* = (\tau_o/\gamma_o) \cos\delta + i(\tau_o/\gamma_o) \sin\delta \quad (2.4)$$

The real and imaginary parts of G^* are defined as storage modulus G' and loss modulus G'' . i.e.

$$G' = (\tau_o/\gamma_o) \cos\delta \quad (2.5)$$

$$G'' = (\tau_o/\gamma_o) \sin\delta \quad (2.6)$$

Storage modulus G' is also called elastic modulus or in-phase modulus, and is proportional to the elastic energy stored in viscoelastic materials, representing the elastic properties of the samples. On the other hand, loss modulus G'' , is also called viscous modulus, or out-of-phase modulus, and is proportional to the dissipated energy, representing the liquid properties of the samples (Macosko 1994).

The magnitude of G^* can be calculated:

$$|G^*| = [(G')^2 + (G'')^2]^{1/2} \quad (2.7)$$

The phase angle (δ) is defined as:

$$\delta = \arctan\left(\frac{G'}{G''}\right) \quad (2.8)$$

For rheological measurements, various geometries are available with their own advantages. The commonly used ones include concentric cylinders (also called coquette), cone-and-plate, and parallel-plates.

2.4.2 Hydrogls

Hydrogels are three-dimensional hydrophilic polymer networks swollen in water (Peppas 1986). Basically, there are two types of hydrogel networks, *i.e.* chemically bonded hydrogels and physical hydrogels. In chemically bonded hydrogels, irreversible links, such as covalent bonds are formed between molecules. On the other hand, the networks of physical hydrogels are held together by physical entanglements of molecules, and reversible secondary molecular interactions, such as hydrogen bonds, charge interactions, and hydrophobic interactions (Berger, Reist et al. 2004; Zhong & Daubert 2004; Hoare & Kohane 2008; Kopecek & Yang 2009). The association of physical hydrogel networks is reversible upon the change of environment conditions, including pH, temperature, ionic strength, stress, and existence of solutes (Kopecek & Yang 2009).

Hydrogel networks can be formed either via self-association of polymers or by adding an appropriate crosslinker. The hydrogel systems composed of two or more types of

molecules are called hybrid hydrogels, such as the hydrogels containing both biological polymers and synthetic polymers (Kopecek & Yang 2009).

Due to their hydrophilicity and biodegradability, natural polysaccharides, such as starches and chitosans, are suitable for preparing hydrogels for some specific applications. Hydrogels can be used for different applications such as food additives, chemical traps, water super-absorbents, water control for oil and gas recovery, drug delivery, tissue engineering, wound dressing, and soft contact lenses (Zhai, Yoshii et al. 2002; Rodríguez, Alvarez-Lorenzo et al. 2003; Hoare & Kohane 2008).

2.4.3 Rheological study on hydrogels

During the process of gelation or crosslinking, when a macromolecule with infinitely large molecular weight appears, the sol-gel transition point is reached (Madbouly & Otaigbe 2005). At the gel point, a sharp change of viscoelastic properties occurs: the system is switched to a solidlike state from a liquidlike state, *e.g.* $G' > G''$. Experimentally, a gel point can be determined by finding the crossover point of the loss modulus and the storage modulus. Another method for determining a gel point was proposed by Winter and Chambon (Winter & Chambon 1986). The criterion is that $G''(\omega)/G'(\omega)$ is independent of frequency at the gel point. However, in some cases, such as the gelation of globular proteins, the moduli near the gelation point are too low to be measured, and the Winter-Chambon method can not be applied. Tobitani and Ross-Murphy suggested to determine gelation points from a point where the storage modulus G' increase rapidly (Tobitani & Ross-Murphy 1997).

During the formation process of hydrogels, the aggregation of physically or covalently bonded chains occurs first, yielding some gel clusters. The gel clusters grow gradually over time, and finally an infinitely large cluster is formed, resulting a 3-dimensional polymer network. The kinetics study on the cluster growth / gelation is of importance for the control of gelation processes. During the process of gelation/crosslinking, the macroscopic physical properties of the system change over time. Therefore, the kinetics of gelation may be studied by monitoring the evolution of the viscoelastic properties of the network (Rodríguez, Alvarez-Lorenzo et al. 2003). An oscillatory rheological test is a nondestruction test due to a small shear strain applied at a low angular frequency. In the past decades, the oscillatory rheological tests have been intensively used for studying the kinetics of various gelation systems, such as cellulose derivatives (Sarkar 1995; Rodríguez, Alvarez-Lorenzo et al. 2003), proteins (Beveridge, Jones et al. 1984; Paulsson, Dejmek et al. 1990; Aguilera & Rojas 1997; Tobitani & Ross-Murphy 1997; Ipsen R, Otte J et al. 2000; Kavanagh, Clark et al. 2000), polyacrylamide (Calvet, Wong et al. 2004), gelatin (Normand, Muller et al. 2000; Nickerson, Patel et al. 2006), poly(lactide-co-ethylene oxide-co-fumarate) (Sarvestani, He et al. 2007), polyurethane (Madbouly & Otaigbe 2005), scleroglucan (Omari 1995), rennet casein (Zhong & Daubert 2004), chitosan (Chenite, Buschmann et al. 2001; Butler, Ng et al. 2003; Lin-Gibson, Walls et al. 2003; Montembault, Viton et al. 2005; Weng, Chen et al. 2007), guar gum (Sandolo, Matricardi et al. 2007), and starch (Eliasson 1986; Doublier & Choplin 1989; Hansen, Hosney et al. 1990; Aguilera & Rojas 1997). Some rheological parameters, such as gel time and gel strength, can be represented as a function of

concentrations and temperatures. Gaunet suggested that for some thermoreversible gels, the modulus is dependent on polymer concentrations with a third power relation (Gaunet 1992).

2.5 Starch nanoparticle preparation and applications

In recent years, preparation and applications of biodegradable nanocrystals/nanoparticles have been attracting more research interests. As a typical biodegradable natural polymer, starch is a good candidate for nanocrystals/nanoparticles. Recently, Le Corre et al. published a comprehensive review on starch nanoparticle preparation, characterization, and applications (Le Corre, Bras et al. 2010). Starch nanoparticles or nanocrystals have many potential applications in various aspects, such as plastic fillers (Angellier, Molina-Boisseau et al. 2005; Angellier, Putaux et al. 2005; Kristo & Biliaderis 2007), food additives (Le Corre, Bras et al. 2010), drug carriers (Simi & Emilia Abraham 2007; Jain, Khar et al. 2008), implant materials (Thielemans, Belgacem et al. 2006), biodegradable composites (Chen, Wei et al. 2008), coating binders (Bloembergen, McLennan et al. 2008), adhesives (Bloembergen, Kappen et al. 2005) and so on. Starch nanoparticles also have a great potential for use in papermaking, surface sizing, paper coating and paperboard as an biodegradable adhesive for substitution of petroleum based adhesives. In addition, starch nanoparticles have many advantages over traditional cooked cationic starches or anionic starches, due to their unique properties such as low viscosities of the suspensions even at a very high solid concentration (up to 30 wt%), and a higher bonding strength (Bloembergen, Kappen et al. 2005; Bloembergen, McLennan et al. 2008).

Starch nanocrystals/nanoparticles can be prepared by three different ways, including acid or enzymatic hydrolysis, regeneration, and mechanical treatments (Le Corre, Bras et al. 2010). Acid hydrolysis is a typical way to generate starch nanocrystals. With acid hydrolysis, platelet-like starch nanocrystals with a length of 20-40 nm and a thickness of 4-7 nm were obtained (Putaux, Molina-Boisseau et al. 2003; Dufresne 2008). The method of acid hydrolysis is difficult for practical applications due to its low yield, a long treatment period, and the use of acid. Nano-sized starch particles can be regenerated by precipitating starch solutions with some organic solvents. Ma et al. used ethanol as a precipitant to precipitate a pre-cooked native starch, and the starch nanoparticles at a size of 50-100 nm were obtained (Ma, Jian et al. 2008). By using a combination of the complex formation with n-butanol and an enzymatic hydrolysis, Kim and Lim prepared starch nanoparticles with a size of 10-20 nm (Kim & Lim 2009). Bastioli et al. filed a patent for producing starch nanoparticles by complexing modified starches with complexing agents followed by mixing with a hydrophobic polymer (Bastioli, Floridi et al. 2009). Starch nanoparticles can also be prepared by processing starch granules with mechanical and thermal treatments. Liu et al. proposed a simple and environmentally friendly method, *i.e.* a high pressure homogenization method for preparing starch nanoparticles (Liu, Wu et al. 2009). Experimentally, 5% starch slurry was passed through a specially designed microfluidizer several times under a high pressure. They found the starch particle size could be reduced from 3-6 μm to 10-20 nm after 20 passes. By combining high-pressure homogenization technique with miniemulsion cross-linking, Shi et al. prepared sodium trimetaphosphate (STMP)-cross-linked starch nanoparticles (Shi,

Li et al. 2011). As a pure mechanical treatment process within a water system, the higher pressure homogenization method is environmentally friendly. However, as only low concentration starch slurry could be processed for homogenization, the efficiency is not high. Another environmentally friendly mechanical method is extrusion. Giezen and coworkers filed a patent of preparing starch nanoparticles via reaction extrusion (Giezen, Jongboom et al. 2000). Basically, the premixed starch and plasticizer were loaded into a twin screw extruder, followed by the addition of reversible crosslinkers, such as glyoxal.. They claimed that the crosslinking via chemical bond formation during the mechanical treatment is an essential step. After the mechanical treatment, partial or even complete cleavage of the crosslinks is realized. The extruded starch particles with a size less than 400 nm were obtained, and the starch nanoparticle suspension at 10% solid content demonstrated a low viscosity of 26 mPas at a shear rate of 55 s^{-1} at room temperature. As extrusion is conducted under semi-dry conditions (approximately at a solid content of 65%), therefore the efficiency is high. The starch nanoparticles prepared by reactive extrusion was also considered as “regenerated starch” nanoparticles because of the crosslinking step (Le Corre, Bras et al. 2010). Based on this technology, a commercial product, Eco-Sphere is produced by Ecosynthetix.

Starch extrusion has been widely investigated by many researchers, particularly in the food industry. During extrusion, starches are subjected to a relatively high pressure, high temperatures and high shear forces. As a result, significant structural changes, including gelatinization, melting, and fragmentation may occur. The physicochemical changes of starches during extrusion were reviewed by Lai and Kokini (Lai & Kokini 1991). It was

noted that, during extrusion, complete gelatinization would not occur because of the limited water content in starches. However, at high extrusion temperatures, starch granules soften and melt, and become more mobile. The softened and melted starch granules are physically torn apart by shear forces so that a faster transfer of water into the interior starch molecules can be achieved. Such mechanical disruption of the molecular bonds by the intense shear force may cause the loss of crystallinity during extrusion. It was found by X-ray diffraction that partial or complete destruction of the crystalline structure of the raw starch granule occurred. This is a good evidence of starch fragmentation during extrusion. During extrusion, the inter or intra- hydrogen bonds between starch molecules can be broken under high shear forces and high temperatures (Lai & Kokini 1991).

The total input of mechanical energy per unit dry weight of extrudate is defined as the specific mechanical energy (SME) (Bhatnagar & Hanna 1994b; Miladinov & Hanna 2000).

$$SME = (2\pi n \tau)/(60 MFR) \quad (2.9)$$

where n is the screw speed (rpm), τ refers to the torque (Nm), MFR represents the mass flow rate (kg/h).

It was found that the molecular weight (M_w) decreased exponentially when the specific mechanical energy input increased (Xie, Yu et al. 2006).

2.6 Paper properties and papermaking processes

Due to a variety of end uses, different paper grades have different property requirements. For most of printing/writing and packaging paper grades, strength properties, such as tensile strength, tear strength, fold endurance, are very important for both the converting processes and the final uses. For example, the speeds of modern printing machines are very high, at the range of 10-15m/s (Murtomaa, Hokkanen et al. 2007). The printing paper must have a high tensile strength to avoid breaking during its traveling on printing machines. Furthermore, stiffness is also an important property for printing/writing paper grades, particularly for copy papers. Low stiffness of paper is one major cause of paper jam during copying and the sheet- fed offset printing (Okomori, Enomae et al. 1999).

The papermaking process is essentially a dewatering process, including draining, pressing and drying. For modern paper machines, machine speeds are getting faster and faster. In order to keep a good runnability of paper machines, higher drainage rates and higher water removal rates during pressing and drying must be achieved. Besides the aspect of improving performance of related equipment, papermaking furnish with a good drainage, pressing and drying properties is also necessary. It is believed that higher drainage rates and water removal rates can be obtained when fibers with low refining levels are used or inorganic fillers are added (Allan, Carroll et al. 1997; Dong, Song et al. 2008; Zhao, Kim et al. 2008; Song, Dong et al. 2009). Unfortunately, the paper strength is relatively low in such situations, particularly for the highly filled grades. Therefore, the paper strength

must be improved, either by adding dry strength agents or via modifications of fibers and fillers.

The fundamental understanding of paper strength has been intensively studied in past decades. Several models on paper strength have also been developed. Based on experimental observations, Page proposed a model for tensile strength (Yoon & Deng 2007). In his model, Page derived the following equation for expressing of tensile strength:

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12}{bPL} \frac{A\rho g}{(RBA)} \quad (2.10)$$

Where T= tensile strength of paper, Z= zero span tensile strength, i.e. fiber strength, A= area of average fiber cross section, ρ = fiber density, g= gravity acceleration, b= shear bond strength per unit bonded area, P= fiber perimeter, L= fiber length, RBA= relative bonded area of sheet

Normally once the pulp type and papermaking conditions are fixed, A, ρ , g, P and L can be considered as constants. Therefore, the tensile strength (T) only depends on the fiber strength (Z), the bond strength per unit bonded area (b) and the relative bonded area (Chakraborty, Sahoo et al.). In order to improve tensile strength, at least one of the above parameters should be increased. Most of approaches developed for improving paper strength target on the increase of bond strength per unit area or relative bonded area, either by adding chemicals or via fiber modifications.

2.7 Applications of starches in the paper industry

Starch is presently the third most prevalent component by weight in papermaking, only surpassed by cellulose fibers and mineral pigments (Maurer 2001). Therefore, the paper industry is one of the most important customers of starch. Currently about 5 million tons/yr of starch are consumed by the global paper industry. Of starches used in the paper industry, about 70 % are in chemically modified forms. The use of modified starches is more common in the United States. Compared to raw starches, modified starches have many advantages, including a greater binding power (the ionic interactions between starches and fibers are stronger than hydrogen bonds), greater stability of molecules and better rheological properties (Jonhed 2006). When using modified starch, a better retention and good runnability can be achieved. Therefore, modified starches not only improve paper qualities, but also increase productivities. In papermaking, starch is used in various areas, including the wet end (papermaking furnish preparation), surface sizing, paper coating, paperboard conversion, and effluent treatments (Maurer 2001; Jonhed 2006). At the wet end of papermaking, starch can be used as a flocculent, retention aid, drainage aid, dry strength additive, and carrier for alkaline size. As an adhesive in surface sizing, starch is used to improve paper surface strengths and dimensional stability. Starch is a typical binder for pigments of coating which imparts smoothness and gloss for high quality printing. Starch is a good adhesive or glue for production of multiply paper boards. Furthermore, cationic starches can also be used to control the discharge of cellulose fibers, pigments, and other furnish components in waste treatments.

Traditionally, starches were used for improving the dry strength of paper and enhancing surface integrity when paper was made primarily from cellulose fibers. Over time, the requirements have changed as papermaking has evolved into a complex process in which nontraditional materials, including recycled fibers, agricultural fibers, mineral fillers, and myriad chemicals are used to improve papermaking processes and functional paper properties of paper. The increase in recycled fiber usage and its recycle times result in the decrease in strength. On the other hand, the market trend is continuing to decrease the basic weight of paper products.

Because native starches are almost nonionic, they are not able to adsorb on fiber effectively. To improve starch adsorption and retention, starches have to be modified, usually to a cationic charge. Modified starches for use as furnish additives are generally substituted products that contain tertiary amino groups, quaternary amino groups, and/or phosphate groups that act as cationic charge carriers. These starches can adsorb onto cellulose fibers and pigments, inducing a patch-type and bridging flocculation, and strengthen the bonding between furnish components.

Both cationic and anionic starches have been used as dry strength agents in papermaking for a long history. The starch must be well cooked before use because uncooked starch is crystal particles which lack bonding abilities with wood fibers. When starches are cooked at a temperature higher than their gelation temperatures, the starch crystals swell and dissolve in water. By adding the soluble starch to pulp slurries, the starch absorbs to fiber surface by either electrostatic forces or van de Waals forces. Although cooked

starches are widely used as papermaking additives, there are many drawbacks. For example, the retention of the cooked starches is based on absorption. Therefore, the absorption amount is limited by saturation adsorption. In other words, papermakers cannot add more starch beyond the absorption saturation limit. Other problems include stick deposit problem caused by unabsorbed starches, slow water drainage rates, over cationics and over flocculation caused by using a high dosage of starches. These negative influences significantly reduce the paper properties and productivities, and increase the energy consumption during papermaking.

A major challenge to use starch as a furnish additive results from the increasing use of recycled fiber for papermaking and the increasing closure of the water systems in paper mills, leading to a ever higher level of dissolved salts and anionic trash in the system. Electrolytes interfere in the retention system. Colloidal trash competes strongly with fibers and pigments for cationic starches. The trash is often hydrophobic and can form undesirable deposits on the paper machine and cause paper-breaks. The main drawbacks for current applied cationic starches are:

- High prices of cationic starches which increase the production cost and restricts their usage;
- Poor retention in the recycled furnish or under high anionic trash conditions;
- A low dosage because of the poor retention;
- Poor paper formation and slow drainage if the cationic starch dosage is over used;
- Limited strength enhancement when the high content of recycled fibers is used.

A concept using uncooked starches was developed in 1950's. The idea was to directly add starch crystal particles to the pulp furnish. These uncooked starch crystals can be easily retained on fiber web by using retention aids. When these retained starch crystal particles move to the dryers, they are swollen under heat, and hydrogen bonds can be formed between the starches and wood fibers. The cost of uncooked starches is much lower than that of cationic starches. This idea was tested in several mills in the early 1950's. However, the tests were failed because the starch particles could not fully swell in paper in paper during drying due to the large particle size of the raw starches. Other problems, such as bright and transparent spots (starch particles) on papers and low opacity were also found.

2.8 Cellulose fiber modifications

Cellulose is a primary structural component of plant cell walls. As a polysaccharide, cellulose is the most abundant natural polymer on Earth. Around 30% of wood fiber components is cellulose. Cellulose is a linear polysaccharide in which the repeated glucose units are bonded together in $\beta(1\rightarrow4)$ linkages (Figure 2.9) (Yoon 2007).

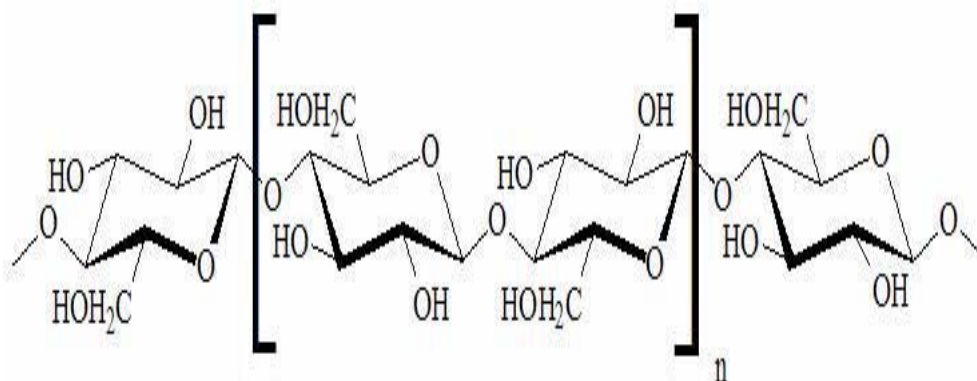


Figure 2.9 Cellulose structure.

Due to their low cost, high strength properties, good processability and biodegradability, cellulose and cellulose fibers have been widely used in various applications, including the support materials for water absorbent (Jain, Xiao et al. 2007), raw materials for textile and paper industry (Biermann 1996), and reinforcing materials for composites (Belgacem & Gandini 2005). The chemical and physical properties of cellulose fibers may be modified so that some desired properties such as water absorbency (Jain, Xiao et al. 2007), strength (Biermann 1996), hydrophobicity (Yang & Deng 2008), thermal resistance (Jain, Xiao et al. 2007), and antimicrobial activity (Guan, Xiao et al. 2007) can be improved.

Modification of cellulose fibers is a very active research area, and numerous methods have been developed in the past decades (Belgacem & Gandini 2005; John & Anandjiwala 2008). Belgacem and Gandini (Belgacem & Gandini 2005) presented a good review in surface modifications of cellulosic fibers. The recent developments in this

area were reported by John and Anandjiwala (John & Anandjiwala 2008). Basically, there are three major types of approaches for fiber modifications, including physical treatments, physico-chemical treatments, and chemical modifications. The purpose of fiber modifications is to create or enhance some certain properties of fiber/fiber products, depending on different applications. Nowadays, fiber modifications have become important practices for many industries, including textile, polymer composite, papermaking, and so forth.

In the paper industry, the modifications of wood pulp fibers have also been intensively investigated. Many physical properties of fibers /papers, such as absorbency, strength, stiffness and water resistance, can be improved by different treatments. In the aspect of paper strength improvement, many fiber modification approaches have been used or proposed (Stamm 1959; Zara, Erdelyi et al. 1995; Biermann 1996; Kling 2001; Pulat & Isakoca 2006; Zheng, McDonald et al. 2006; Lvov, Grozdits et al. 2007; Rahman & Khan 2007; Zhang & Ragauskas 2007; Wang & Deng 2008) .

As a physical treatment, refining is one of the most common methods for improving paper dry strengths (Biermann 1996). After refining, fibers become more flexible. The contact areas (i.e. bonding areas) among fibers can be significantly increased due to the wood fibrils on fiber surface generated during refining. Therefore, the total fiber bonding strength can be improved. Although refining can significantly improve paper strength properties, such as tensile strength, z direction strengths (ZDT), folding endurance, etc.,

the stiffness of paper is sacrificed, and large amount of fines are generated. Furthermore, the energy cost of refining is very high.

The chemical methods for fiber modifications mainly include fiber wall crosslinking (Stamm 1959; Zhou, Luner et al. 1995), layer-by-layer (LbL) nanocoating technology (Zheng, McDonald et al. 2006; Lvov, Grozdits et al. 2007) and grafting of polymers onto fibers (Kamdem, Riedl et al. 1991; Gupta, Sahoo et al. 2002; Loría-Bastarrachea, Carrillo-Escalante et al. 2002; Abu-Ilaiwi, Ahmad et al. 2004; Belgacem & Gandini 2005; Coskun, Mür et al. 2005; Fan, Zhao et al. 2006; Pulat & Isakoca 2006; Guan, Xiao et al. 2007; Jain, Xiao et al. 2007).

Fiber wall crosslinking was studied by several researchers (Stamm 1959). It was found that the dimensional stabilization of paper could be improved by crosslinking fiber wall with formaldehyde. Kling (Kling 2001) used butanetetracarboxylic acid (BTCA) to crosslink fiber wall, aiming to obtain stiffer fibers.

The layer-by-layer (LbL) nanocoating technology was applied by many researchers to modify fibers. Zheng and coworkers (Zheng, McDonald et al. 2006) produced negatively and positively charged fibers via alternate adsorption of positive and negative polyelectrolytes. The tensile strength of paper made of the LbL-treated fibers was significantly increased, compared to the paper made of the untreated fibers. Lvov et al. (Lvov, Grozdits et al. 2007) also applied a layer-by-layer technology to treat recycled fibers and the paper strength properties were increased. Wang and Deng utilized a semi-

layer-by-layer approach with CMC-cationic complex to modify fiber surfaces, resulting in an increased paper strength (Wang & Deng 2008).

In-site polymerization of monomers in the presence of cellulose fibers has been intensively investigated by many researchers. By using appropriate initiation techniques, such as UV irradiation, plasma irradiation, gamma ray irradiation, and redox initiation with manganese or ceric (IV) ion, free radicals can be generated on the cellulose molecules, and then monomers can be grafted onto cellulose fibers. Various monomers, such as methyl acrylate (Abu-Ilaiwi, Ahmad et al. 2004; Jain, Xiao et al. 2007), ethyl acrylate (Gupta, Sahoo et al. 2002), acrylic acid (Loría-Bastarrachea, Carrillo-Escalante et al. 2002), methyl methacrylate (Kamdem, Riedl et al. 1991), acrylamide (Fan, Zhao et al. 2006), styrene (Coskun, Mür et al. 2005), vinyl acetate and methacrylamide (Pulat & Isakoca 2006), have been used for grafting of polymers onto cellulose fibers. Grafting of polymers onto fibers for improving paper properties was also intensively investigated in the past decades. Zara and coworkers (Zara, Erdelyi et al. 1995) investigated the grafting of cellulose with vinyl acetate monomers. Pulat and Isakoca (Pulat & Isakoca 2006) studied graft copolymerization of vinyl monomers onto cotton fibers. Rahman and Khan (Rahman & Khan 2007) grafted ethylene dimethylacrylate (EMA) on coir fibers, and the tensile strength of fibers was increased. However, there are some drawbacks related to the free radical polymerization technique, such as complex and rigorous reaction conditions, long reaction time, high costs of chemicals and environmental concerns (Roche 2006). Normally the obtained products from the free radical polymerization grafting are a mixture of grafted polymers, ungrafted homopolymers, and unreacted

monomers. Non-water solvent is commonly involved in free radical polymerization process. The unreacted monomer residues are usually toxic. The purification of the products is a difficult and energy consuming process. In order to remove the monomers and ungrafted homopolymers, the grafted products are often washed with a large amount of water or extracted with solvents for more than 24 hours. Consequently, the final products after extraction are completely denatured, and become nonfibrous cellulose (Roche 2006). Furthermore, the reaction time for graft copolymerization was normally very long, requiring several hours, which is not suitable for some industry applications, such as papermaking.

Instead of free radical polymerization with monomers, directly grafting commercial available polymers onto cellulose fibers by simply adsorption or layer by layer self-assembly has also been reported (Roche 2006). For example, cationic polymers can be physically grafted onto fiber surfaces via electrostatic adsorption, because cellulose fibers have a negative surface charge. By adsorbing cationic polyacrylamide with fibers, Roche (Roche 2006) prepared a polycation grafted cellulose fibers which could be used as a retention aid. Although the simple adsorption method can physically attach polymers on fibers, the maximum adsorption amount is limited by the saturation of adsorption. The low amount of polymer grafting sometimes cannot satisfy certain applications. For example, grafting of superabsorbent on wood fibers is a technique that has been widely used in the diaper industry. For this application, large amount of polymers need to be grafted on fiber surface. On the other hand, anionic or non-ionic polymers may be

chemically grafted onto cellulose fibers by using appropriate crosslinkers or couple agents.

Furthermore, fiber charge enhancement is also an effective means to improve paper strengths. Zhang and Ragauskas (Zhang & Ragauskas 2007) found that the paper dry-tensile stiffness of paper could be significantly increased when the fiber surface charge was increased via catalytic oxidation of unbleached softwood kraft pulp.

2.9 Filler modification

It is a common practice for today's paper industry to add mineral fillers to replace part of fibers, particularly in printing and writing paper grades. Actually, filler is the second most used materials of papermaking. There are three major benefits for papermakers to use fillers. Firstly, the cost of raw materials can be reduced because of the low cost of mineral fillers. Secondly, the papermaking process, such as water drainage, wet pressing and drying can be improved with the addition of fillers (Allan, Carroll et al. 1997; Zhao, Kim et al. 2008). Thirdly, some desired paper properties can be obtained, such as a high opacity and better printing performance. Unfortunately, the strengths of paper with fillers would be decreased because filler particles can interfere fiber-fiber bonding. The low retention of fillers is another concern for papermakers.

In order to increase the retention and bonding capability of fillers, pretreatments or modifications have to be conducted. Many technologies have been developed in the past decades. The filler pre-flocculation technology was intensively investigated by many

researchers (Smith 1981; Park & Shin 1987; Mabee & Harvey 2000; Mabee 2001). Basically, flocculant agents are mixed with fillers first before adding into fiber slurries. Normally the pretreated fillers have an increased particle sizes and an enhanced surface charge. With this technology, the filler retention can be significantly increased, and there is no loss of paper strength. Filler modification by polymer coating is a popular topic for researchers (Novak, Stark et al. 1987; Dunham, Jakubowski et al. 1999; Koper, Vanerek et al. 1999; Vanerek, Alince et al. 2000). Poly acrylic acid, poly vinyl acetate, epichlorohydrin, polyamine, polyamino-amide and cationic starches were commonly used polymers for pretreatment of fillers.

Furthermore, Aho and coworkers (Aho, Silenius et al. 2006) found that the strength of paper could be increased when using filler and wood fines composites. Filler Lumen loading methods were also studied by many researchers (Green, Fox et al. 1982; Middleton & Scallan 1985; Miller & Paliwal 1985). Large amount of filler particles can be loaded into fiber lumen either by mechanical methods or by chemical deposition.

Recently a novel concept of filler modification via starch coating was proposed by Deng's group at Georgia Tech (Yan, Liu et al. 2005; Zhao, Hu et al. 2005; Yoon & Deng 2006a; Yoon & Deng 2006b; Zhao, Kim et al. 2008). Basically, a very thin layer of starch can be coated on the surface of filler particles/aggregates either by wet approaches or by dry approaches. There are two major advantages to apply these approaches: one is the low cost because of using raw starch; the other one is enhanced filler-filler and fill-fiber bonding. Yoon and Deng (Yoon & Deng 2006a; Yoon & Deng 2006b) developed a

series of wet approaches to coat fillers with starches, including starch-clay composite by $(\text{NH}_4)_2\text{SO}_4$ and starch-clay composite by fatty acid complex. The fatty acid-starch complex method is a very simple, effective and practical method of filler modifications for the paper industry. Tensile strength of paper could be increased up to 200%. Yan (Yan, Liu et al. 2005) and Zhao et al. (Zhao, Hu et al. 2005) coated starch on clay and PCC particles via a vacuum dry and grinding method, and the paper strength was considerably increased. Zhao and coworkers (Zhao, Kim et al. 2008) also applied a spray dry method to coat clay fillers with cooked raw starches. Both the lab and pilot trial results showed significant improvements of paper strength and energy saving of pressing and drying.

CHAPTER 3

RESEARCH OBJECTIVES

Starch crosslinking has been used in paper coating, filler modification, papermaking retention aid and dry strength agent developments. In paper coating, crosslinkers, such as ammonium zirconium carbonate (AZC), are used as insolubilizers to crosslink the starch in the coating film. However, the mechanisms involved in AZC-starch crosslinking have not been well understood. In order to optimize the current processes of paper coating and find new paths for the utilizations, such as the fiber modification developed in this study, a fundamental understanding of the AZC-starch crosslinking chemistry and physics is necessary.

Starch crosslinking has also been employed in the preparation of starch nanoparticles, and it was found that the addition of some crosslinker agents is important. However, there is no report about why and how the crosslinker can improve the process of nanoparticle formation.

This thesis work accomplished three major objectives. First, a better understanding of starch-AZC crosslinking in an aqueous solution and related crosslinking kinetics was obtained. Second, new application of the starch-AZC crosslinking in fiber surface modification was developed, and the related mechanisms were investigated. Third, the mechanism of starch nanoparticle formation during extrusion with crosslinkers was studied in detail.

Mechanistic study of starch crosslinking induced by AZC

The main objective of this part of the work was to study the mechanism and kinetics of AZC self-crosslinking and AZC-starch co-crosslinking. The specific objectives include the following:

- 1) observe the sol-gel transition for AZC self-crosslinking and AZC-starch co-crosslinking via inversion tests;
- 2) monitor the evolution of viscoelastic properties of the AZC solution and the AZC-starch blends by using rheological measurements;
- 3) determine the dependence of the bond formation rate and the gel strength on AZC and starch concentrations;
- 4) determine the temperature dependence of the bond formation rate and the gel strength;
- 5) investigate the effect of solution pH on the crosslinking process;
- 6) study the reaction of AZC self-crosslinking and AZC-starch co-crosslinking by tracking the release of CO₂ over time.

Fiber and filler modifications with starch and crosslinkers

To graft the low-cost native starch directly onto fibers is a promising pathway to improving fiber-fiber bonding, and thus improving paper strength. It has been reported that ammonium zirconium carbonate (AZC) can react with both starch and cellulose by forming hydrogen bonds. The main objective of this part of work was to develop a new

method of fiber modification via starch grafting by using AZC as a coupling agent. The specific objectives are to:

- 1) investigate the effects of reaction conditions, including temperature, pH, starch and AZC dosage, fiber consistency, and stirring speed on the starch grafting efficiency on fibers;
- 2) determine the effect of starch grafting on the water retention value of fibers;
- 3) investigate the effect of starch grafting on water drainage and the water removal rate in the wet web press and paper drying section;
- 4) study the effect of starch grafting on the physical properties of paper;
- 5) study the repulping of dry pulp board made of starch grafted fibers; and
- 6) evaluate the strength properties of paper made of the repulped starch grafted fibers.

In order to improve the filler-fiber bonding capability, a series of simple and effective filler modification approaches based on the starch coating on fillers have been successfully developed in recent years. However, the starch-coated filler particle aggregates are not stable in water and are likely to break up. In this study, a concept of using starch-crosslinking to improve the stability of starch modified filler in water was developed and tested. The results indicate that the crosslinking of the modified starch layer is not necessary.

Mechanism of starch nanoparticle formation during extrusion with crosslinkers

Reactive extrusion is an effective and environmentally friendly approach to the preparation of starch nanoparticles. It is reported that starch crosslinking is an essential step for producing starch nanoparticles. However, it is not clear why and how the crosslinker agent can reduce the starch particle size during extrusion. It is well known that crosslinking can increase the molecular weight of materials, and an enhanced network structure is usually obtained. How the starch particle size can be reduced to nano size within an extruder with a millimeter gap is fundamentally interesting. The main objective of this part of the work was to investigate the mechanism of starch particle size reduction during extrusion with and without crosslinkers by identifying the contributions of thermal energies and mechanical forces.

CHAPTER 4

RHEOLOGICAL STUDY OF SELF-CROSSLINKING AND CO-CROSSLINKING OF AMMONIUM ZIRCONIUM CARBONATE AND STARCH IN AQUEOUS SOLUTIONS

Abstract

In this chapter, the self-crosslinking of ammonium zirconium carbonate (AZC) and its co-crosslinking with starch in aqueous solutions were investigated using rheological measurements. The evolution of viscoelastic properties of AZC solutions and AZC-starch mixtures was characterized, and the crosslinking kinetics was determined. It was found that for both AZC self-crosslinking and AZC-starch co-crosslinking, the initial bond formation rate and the gel strength exhibit a power law scaling with polymer and crosslinker concentrations. The results indicate that the development of the crosslinking network strongly depends on the AZC concentration but less depends on starch concentration. The temperature dependence of crosslinking was described by the Arrhenius plots which demonstrate a good linearity. It was determined that the activation energy of AZC self-crosslinking was approximately 145-151 kJ/mol, and the activation energy of AZC-starch co-crosslinking was 139 kJ/mol. The effect of solution pH on the crosslinking process was also studied.

4.1 Introduction

Ammonium zirconium carbonate (AZC) is a common crosslinker for starch, and it has already been widely used as an insolubilizer in paper coatings (Wolff, Calcar et al. 1996; Ryu, Gilbert et al. 1999). The reaction mechanism depicted in Figure 2.7 (in chapter 2) suggests that AZC can react with polymers containing hydroxyl groups by forming hydrogen bonds, such as starch and cellulose (Farnworth, Jones et al. 1981). The crosslinking reaction can also occur between AZC molecules. Although the chemistry and applications of AZC has been studied intensively, the kinetics of AZC self-crosslinking and AZC-starch interactions have not been studied. Improved understanding of AZC-starch crosslinking is a prerequisite for further optimizing existing processes in paper coating, surface sizing, fiber modification and other applications.

When aqueous AZC solutions (one component system) are heated, the AZC molecular structure changes: CO_2 and NH_3 are released, while new hydrogen bonds are formed via inter- and intramolecular interactions (Figure 2.7). As a result of this self-association, a crosslinked hydrogel network can be formed, which will be referred to as a heat-induced AZC gel in this report. For precooked starch solutions at a low starch concentration (less than 3% by weight), self-association between starch molecules is not sufficient to form a hydrogel network. In order to obtain a crosslinked polymeric network in these dilute solutions, a crosslinker like AZC has to be induced. With the addition of AZC in a starch slurry, interchain hydrogen bonding occurs between starch molecules, and a crosslinked starch hydrogel network can be formed. In blends of AZC and starch, both AZC self-

crosslinking and AZC-starch co-crosslinking can occur at elevated temperatures. Therefore, unlike other common polymer-crosslinker systems, AZC-starch gels are expected to contain two types of networks, *i.e.* heat-induced AZC networks and AZC-crosslinked starch networks. In order to develop a thorough understanding of the formation of these mixed gels, studies on the formation of the individual gels should first be conducted.

The classical theory of rubber elasticity (Pearson & Graessley 1980; Prud'homme 1984; Omari 1995; Sarkar 1995; Zhong & Daubert 2004) predicts that the network modulus is proportional to the bond density, *i.e.*

$$G = q v k T + G_o \quad (4.1)$$

Where q is a coefficient between 0.4 and 1 (Omari 1994), v is the bond density, k is the Boltzmann constant, and T is the absolute temperature. G_o represents the initial modulus of polymers before gelation. Essentially, G_o is the contribution of chain entanglement to modulus, and is normally a very small value.

From equation 4.1, it can be seen that the gel strength G is proportional to the bond density. The time derivative of equation 4.1 can be written as:

$$dG/dt = q k T dv/dt \quad (4.2)$$

The above expression shows that the rate of modulus change is proportional to the rate of bond formation at a given temperature (Prud'homme 1984). Therefore, tracking the changes of modulus can provide us with some inherent information about bond formation in the network of interest. The bond formation rate is expected to depend on polymer and crosslinker concentrations, and on reaction conditions like temperature and pH. Power-law scaling between bond formation rates and concentration has been reported in the literature, but the values of the scaling exponent were found to vary with reaction systems and conditions (Omari 1994). The scaling exponents with respect to the crosslinker concentration, 2.1, 4/3, and 1 were reported for the polyacrylamide-glyoxal system (Omari 1994), the hydroxypropyl guan-titanium (Clark & Barkat 1989), and the scleroglucan-zirconium system (Han 1992) respectively. The scaling exponents with respect to the polymer concentration, 2.7, 1.4 and 2/3 were reported for the polyacrylamide (Omari 1994), scleroglucan-zirconium system (Omari 1995) and the hydroxypropyl guan-titanium (Clark & Barkat 1989) respectively.

The temperature dependence of reaction rates can be described by the Arrhenius equation (Colby, Osaka et al. 1988):

$$k = A \exp (-E_a/RT) \quad (4.3)$$

where A is the pre-exponential factor, E_a refers to the experimental activation energy, R is the gas constant, and T is the absolute temperature.

For the crosslinking/gelation process, the reaction rate is essentially proportional to the change rate of rheological parameters, i.e. dG/dt . Therefore, the rheological parameter change rate dG/dt , rather than the reactant concentration change rate, can be used to express the reaction rate in the Arrhenius equation (4.3) (Ahmed, Ramaswamy et al. 2008):

$$dG/dt = A \exp (-E_a/RT) \quad (4.4)$$

Ahmed et al. determined the activation energy E_a of basmati rice starch by utilizing the above relationship (Ahmed, Ramaswamy et al. 2008).

In some cases, the dG/dt is hard to be determined. On the other hand, as gelation is a polycondensation process, and the drastic change of moduli allows to determine the gelation point (Madbouly & Otaigbe 2005). The reaction rate can be characterized as the inverse of the gelation time. A new form of the Arrhenius equation can be obtained:

$$1/t_{gel} = A \exp (-E_a/RT) \quad (4.5)$$

By using the above equation, the values of activation energy of gelation for different polymer systems, such as silicon alkoxides (Colby, Osaka et al. 1988), polyacrylamide (Han, Muller et al. 1997), chitosan (Weng, Chen et al. 2007), gelatin (Nickerson, Patel et al. 2006), sunflower globulin hydrolysates (Sanchez & Burgos 1997) were determined.

The objective of this chapter was to study the mechanism and kinetics of AZC self-crosslinking and AZC-starch co-crosslinking by monitoring the evolution of the modulus for AZC solutions and AZC-starch blends. Power-law scalings for the initial bond formation rate and the gel strength were determined as a function of starch and AZC concentration. The temperature dependence of crosslinking was described by an Arrhenius expression, and the activation energy values of AZC self-crosslinking and AZC-starch co-crosslinking were determined. The effect of solution pH on the crosslinking process was also studied.

4.2 Experiments

4.2.1 Materials

Native corn starch (B200) was provided by Grain Process (Muscatine, Iowa USA). Starch suspensions at 1-3% solid content by weight were precooked at 95°C for 40 minutes using a rotary evaporator. An ammonium zirconium carbonate aqueous solution containing 1-2% tartaric acid as stabilizer was purchased from Aldrich, USA.

4.2.2 Methods

Turbidity test and CO₂ release tests

The turbidity of polymer solutions was measured with a Digital Direct-Reading Turbidimeter (Orbeco-Hellige, Sarasota, Florida). The amount of carbon dioxide release

during gelation was determined using a multisampling method with headspace gas chromatograph. Details about the multisampling method can be found in a previous publication (Chai, Dong et al. 2008).

Rheological characterization

Rheological measurements were conducted by using an MCR 300 controlled stress rheometer (Anton Paar) with a standard couette geometry (CC17: the inner diameter of the cup is 18.08 mm and the diameter of the bob is 16.66 mm.) in small deformation oscillatory mode. A predetermined amount of the crosslinker (AZC solution) was mixed with 20ml DI water or starch solution at room temperature and pH was adjusted to the desired value with 5% NaOH solution or 5% HCl solution. After stirring for 5 minutes, 4.72 ml sample was transferred into the measuring cup of the rheometer. A thin layer of low viscosity silicon oil was applied on the top of sample in order to prevent moisture losses during measurements at high temperatures. Storage moduli G' and loss modulus G'' were measured over time at a frequency of 1 Hz and a strain amplitude of 5%, which was within the linear viscoelastic regime for all samples.

4.3 Results and Discussion

As a crosslinking agent, AZC can react with polymers containing hydroxyl groups (Figure 2.7). Similarly, with relatively large number of hydroxyl groups in its molecule, self-assembly between AZC molecules can also occur. Therefore, in a one-component system of AZC solutions, AZC self-crosslinking can occur. In a two-component system

of AZC-starch blends, both AZC self-crosslinking and AZC-starch co-crosslinking exist, and these two associations might compete with each other. For a qualitative study, some visual observations were conducted. For the quantitative investigation, the crosslinking (or gelation) process was characterized using turbidity tests and rheological measurements.

4.3.1 Visual observation

At elevated temperatures ($> 60^{\circ}\text{C}$), the crosslinking between individual AZC molecules can result in a weak hydrogel. The gel strength, corresponding to the degree of crosslinking, is highly dependent on the reaction temperature and AZC concentration in solutions. Figure 4.1 demonstrates different samples in inverted vials. After 1 hour reaction time at 60°C , the initially clear AZC solution with low concentrations (2,000 ppm and 6,000 ppm) become sticky and opaque, but no stable gel was formed (Figure 4.1 a, b). At a higher concentration of 10,000 ppm (Figure 4.1c), a stable gel was formed. If a higher reaction temperature (70°C) was applied, the 6,000 ppm AZC sample could also be converted to stable gel after 1 hour (Figure 4.1d).

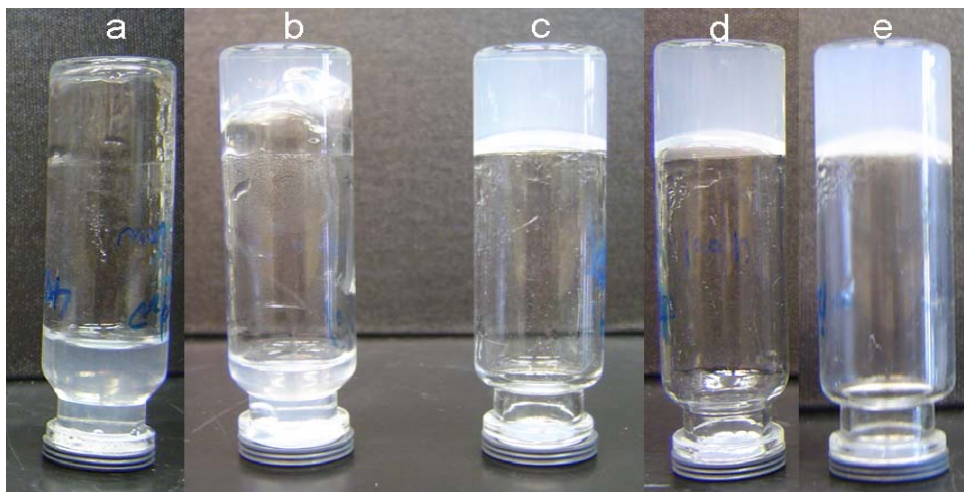


Figure 4.1 3-hour inversion tests for different samples (reaction 1 hour at 60°C: a. 2000 ppm AZC in water; b. 6000 ppm AZC in water; c. 10,000 ppm AZC in water; reaction 1 hour at 70°C: d. 6000 ppm AZC in water, e. 6000 ppm AZC in 1% starch).

If AZC is added to a starch solution, there are two competitive crosslinking reactions: AZC self-crosslinking, and AZC-starch co-crosslinking. With the involvement of AZC-starch co-crosslinking, whether an enhanced gel network can be achieved is one concern for this study. The inversion test result shows that a stable hydrogel was also formed for the AZC-starch mixture (Figure 4.1 e).

4.3.2 Turbidity test

The initial AZC solutions at room temperature were clear. With the proceeding of crosslinking upon heating, the solutions became turbid. As shown in Figure 4.2, the turbidity of the samples increased first, and then leveled off. Turbidity is a visual reflection of the crosslink process, which apparently leads to microscopic phase separation. It was also found that for the same reaction times, the higher the AZC concentration, the higher the turbidity of the crosslinked gels.

As the precooked starch used in this study is not a clear solution initially, the turbidity test for AZC-starch mixtures was not applicable.

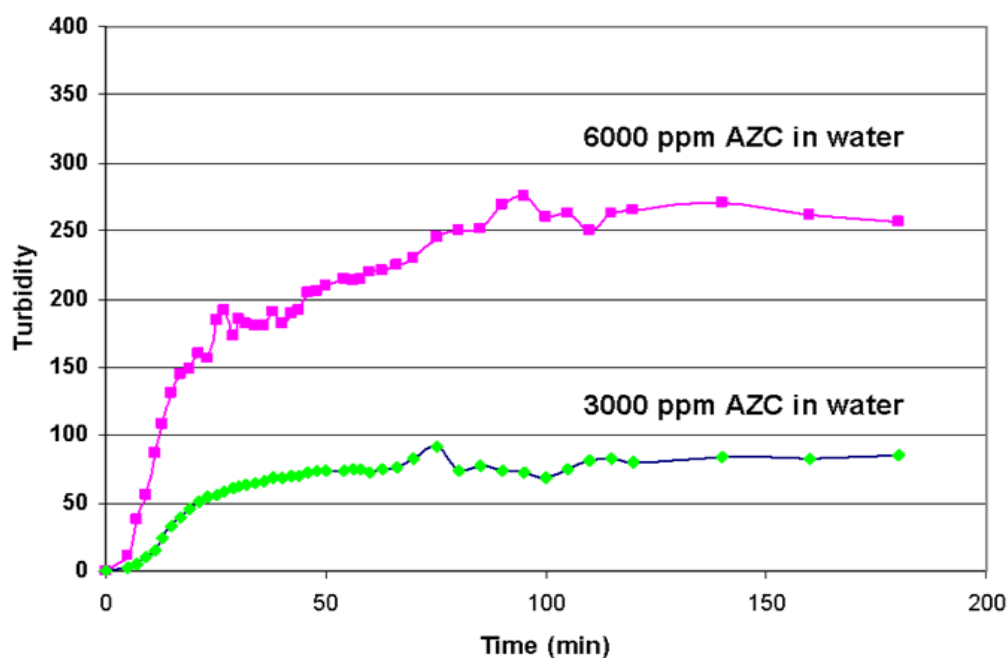


Figure 4.2 The change of turbidity during the process of AZC self-crosslinking at 80°C.

4.3.3 Rheological characterization

4.3.3.1 Starch self-association

One objective of this study is to investigate the network of starch crosslinked by AZC. Before conducting the study on the two-component system, the self-association of the starch in aqueous solutions was investigated to provide a benchmark.

It is well known when uncooked starch slurries are heated to an elevated temperature (80-90°C), a significant viscosity increase occurs due to the swelling of starch granules. The viscoelastic behavior of uncooked starches during heating has been studied extensively and some kinetic models have been established (Kokini 1992; Aguilera & Rojas 1997). In this study, the starch samples used are precooked starches. The rheological properties, including loss modulus and storage modulus, were determined by applying small amplitude oscillatory rheological tests. Figure 4.3 represents the evolution profiles of the moduli for a starch solution at 80°C. It can be seen that both the loss and storage moduli remained virtually constant at low values, indicating the lack of measureable changes of rheological properties over time. In other words, the self-association of starch molecules in such a dilute solution is negligible and can be neglected when AZC is added as a crosslinking agent.

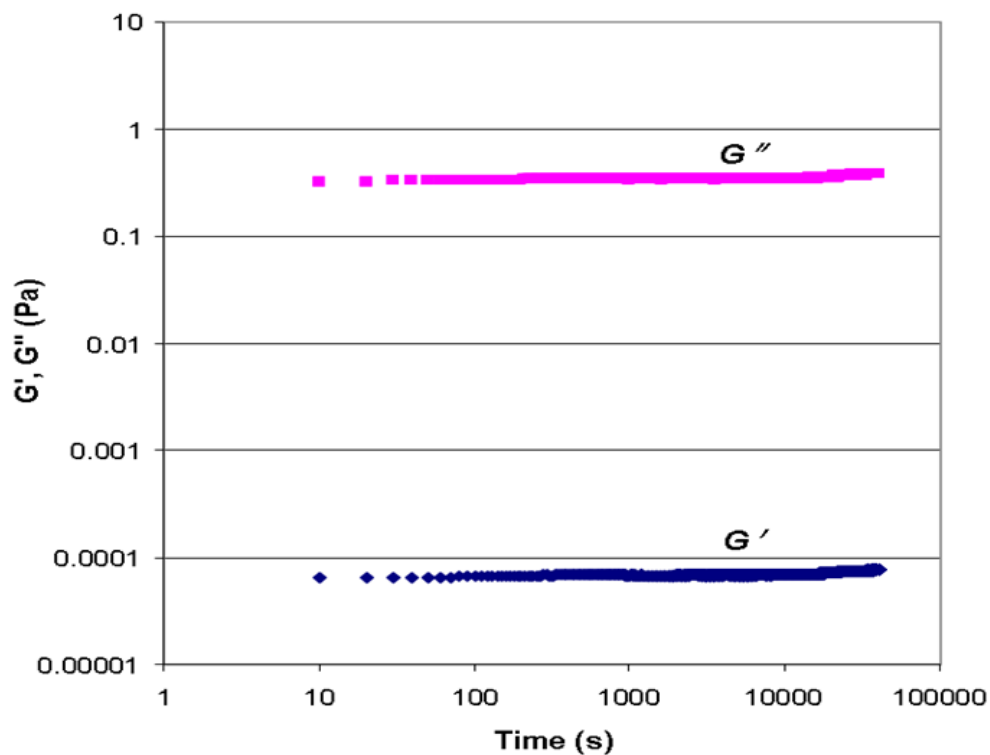


Figure 4.3 Evolution of rheological properties of a precooked starch solution (10000 ppm starch solution at 80°C).

4.3.3.2 AZC self-crosslinking

Time sweep profiles of loss modulus and storage modulus

The evolution of rheological properties was monitored for AZC solutions with different concentrations (600-4500ppm) at 80°C, and the time sweep profiles are summarized in Figure 4.4.

From the profiles we can see that at the initial point regardless the AZC concentrations, the loss modulus G'' was larger than the storage modulus G' , indicating a liquid status of the system. With the proceeding of reaction, different behaviors occurred for different AZC concentrations. At a low AZC concentration (600 ppm Figure 4.4a), there was only

very slight increase of moduli. For the 1500 ppm AZC solution (Figure 4.4b), both loss modulus and storage modulus increased first, and then leveled off to a certain value. The storage modulus was still much smaller than loss modulus, indicating no gel was formed. For the 2250 ppm AZC solution (Figure 4.4c), after around 900s, both the loss modulus and the storage modulus increased rapidly. At around 3900s the cross-over of the storage modulus and the loss modulus occurred. The cross-over point of the storage and loss modulus is normally called a gel point (Kavanagh & Ross-Murphy 1998; Nickerson, Patel et al. 2006). The time to reach this point is called the gel time. After the gel point, both the storage modulus and the loss modulus kept increasing until reaching a level-off value. The data also show that the values of the storage modulus G' were much larger than those of the loss modulus G'' , indicating that the elastic properties were dominant. Basically, the whole profile presents a typical rheological property change for gel formation. A similar profile (Figure 4.4d) presents for the system with 4500 pm AZC concentration, but the gel time (860s) were much shorter. Therefore, for the form of AZC hydrogel at 80°C, a critical concentration should be around 2250 ppm. When the AZC concentration was below this level, no gel could be formed.

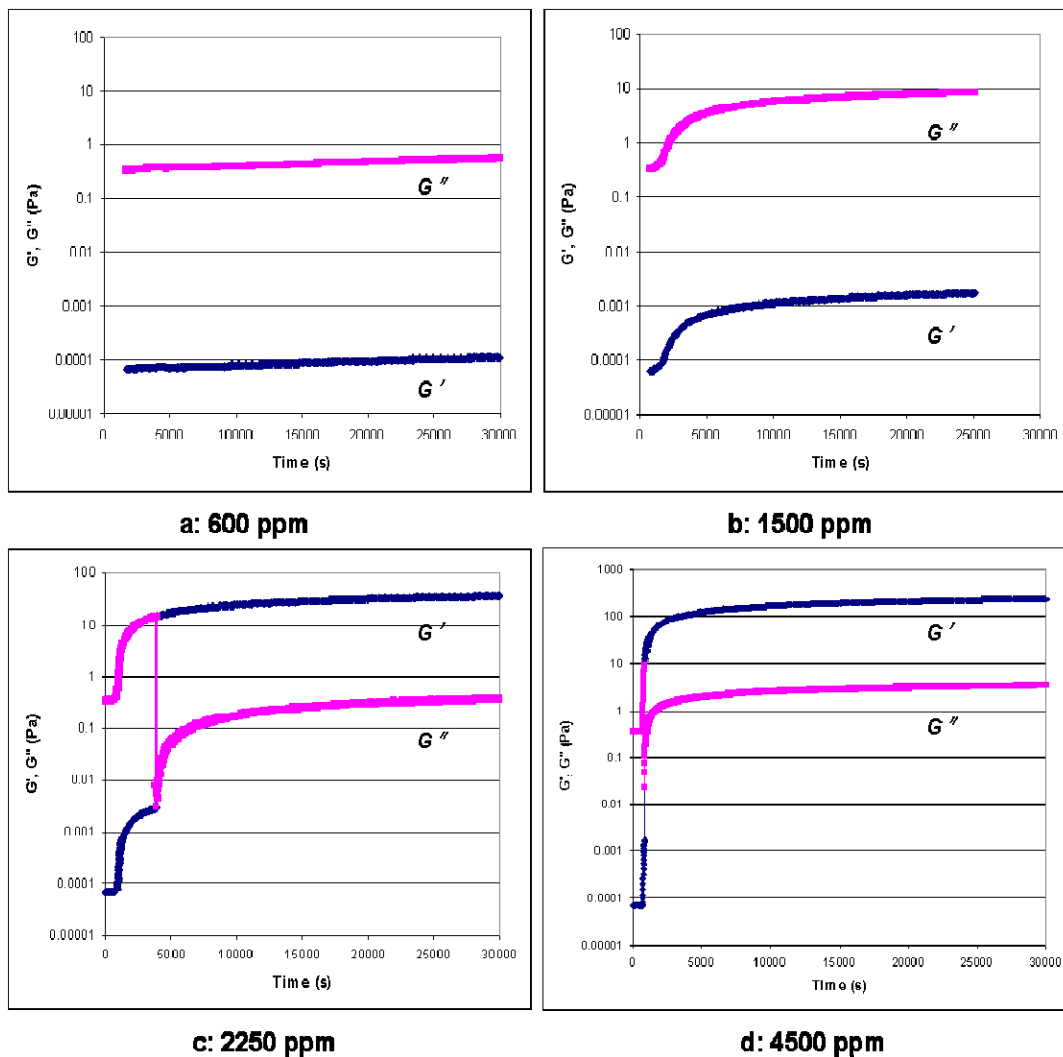


Figure 4.4 Time sweep profiles of AZC self-cross-linking for the AZC solutions with different concentrations (80°C, pH 9).

However, an unusual phenomenon was observed around the gel point (Figure 4.4 c, d), i.e. a sharp increase of the storage modulus and a sharp decrease of the loss modulus were involved, which is not reasonable for a typical gelation process whose modulus curves demonstrate smooth changes of modulus before and after the gel point. The possible reasons for causing such sharp changes were studied. In aspects of the geometry of measurements, both the cone-plate geometry and the couette geometry were used, and

similar results were obtained. In addition, the initial AZC solutions for the rheology tests are clear homogeneous solutions, which means the effect of big clusters in samples does not exist. Although more studies are needed, our observation indicated that the gas bubbles (CO_2 and NH_3 generated during the crosslinking reaction) may be one of the possible reasons.

Gas bubble effect

For normal crosslinking process, there is no gas generated, and the air amount in initial samples can be neglected. However, for the AZC crosslinking system, both CO_2 and NH_3 are generated during the reaction, and entrapped in the solution/gel as small bubbles (Figure 4.5).

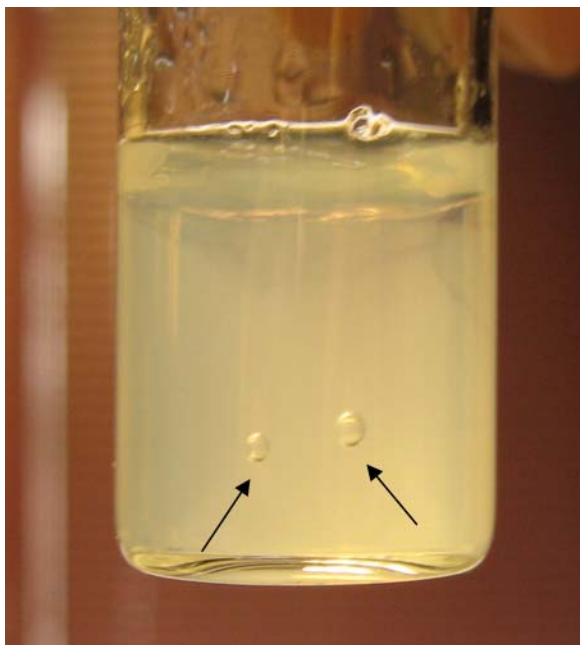


Figure 4.5 Entrapped gas bubbles in the AZC self-crosslinked gel

In order to investigate the effect of the bubbles on rheological properties of the samples, a series of air bubble simulation tests were conducted. Basically, 4-6 small air bubbles (around 10 μ l air was injected by using a syringe with a long needle to form a bubble in the gel) were introduced in the measured samples at different stages of the gelation. When air bubbles were introduced in a polyvinyl alcohol (PVA) solution with a high viscosity at room temperature, the storage modulus had a sharp increase, while there was almost no change for the loss modulus (Figure 4.6). This result illustrates the effect of bubbles on viscoelastic properties of fluids. The effect of air bubbles on gelation process was also studied. Basically, the crosslinking process was stopped at an early time (before the crossover point of the loss and storage modulus) by quenching the sample to 25°C, and then air bubbles were introduced into the samples (Figure 4.7 and 4.8). The choice of a reaction stopping time is critical. In case 1 (Figure 4.7), the reaction was stopped at 1100s. After introducing air bubbles, a sharp increase of the storage modulus and a sharp decrease of the loss modulus occurred, and the crossover point was also observed. However, after a short time (about 200s), both the two modulus quickly switched back to their initial values. This is because the entrapped air escaped from the sample which did not have a high enough viscosity to hold the air bubbles. When the air bubbles were introduced at a later time (around 1300s in Figure 4.8), the sharp crossover of the storage modulus and the loss modulus also happened, and the moduli did not switch back again. These simulation results confirmed the existence of bubble effects during gelation process.

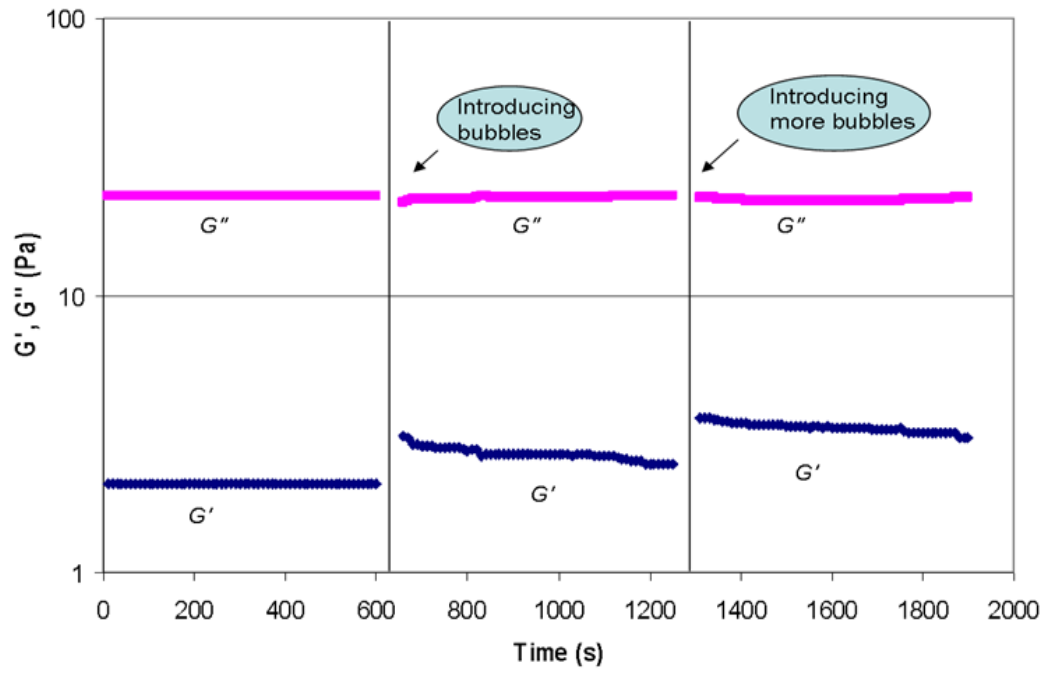


Figure 4.6 Effect of air bubbles on the rheological property change of a PVA solution with a high viscosity.

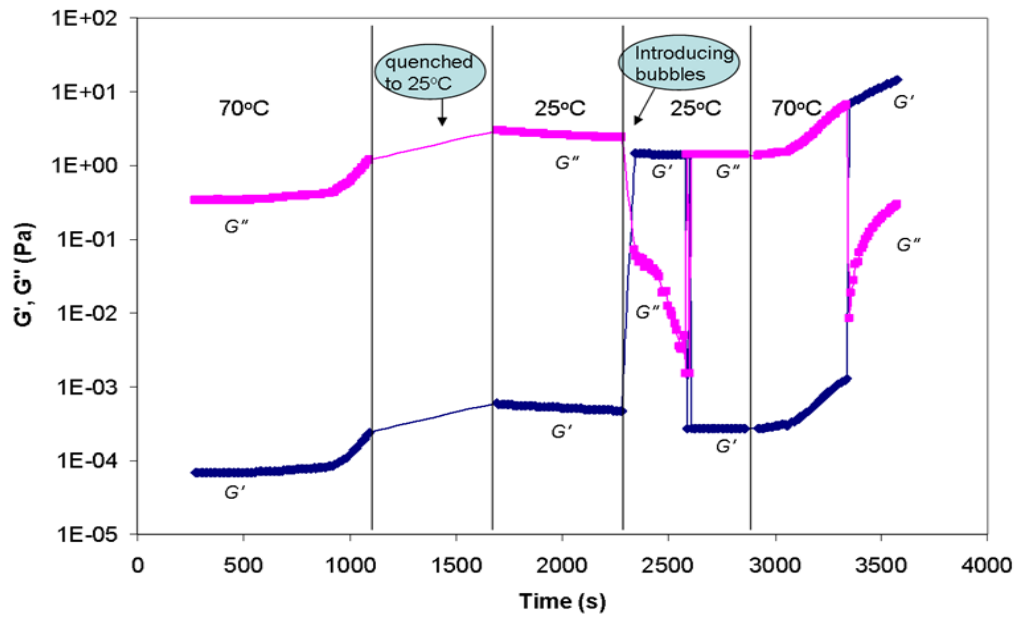


Figure 4.7 Effect of air bubbles on the rheological property change of a AZC solution (24000 ppm AZC in water at 70°C): case 1.

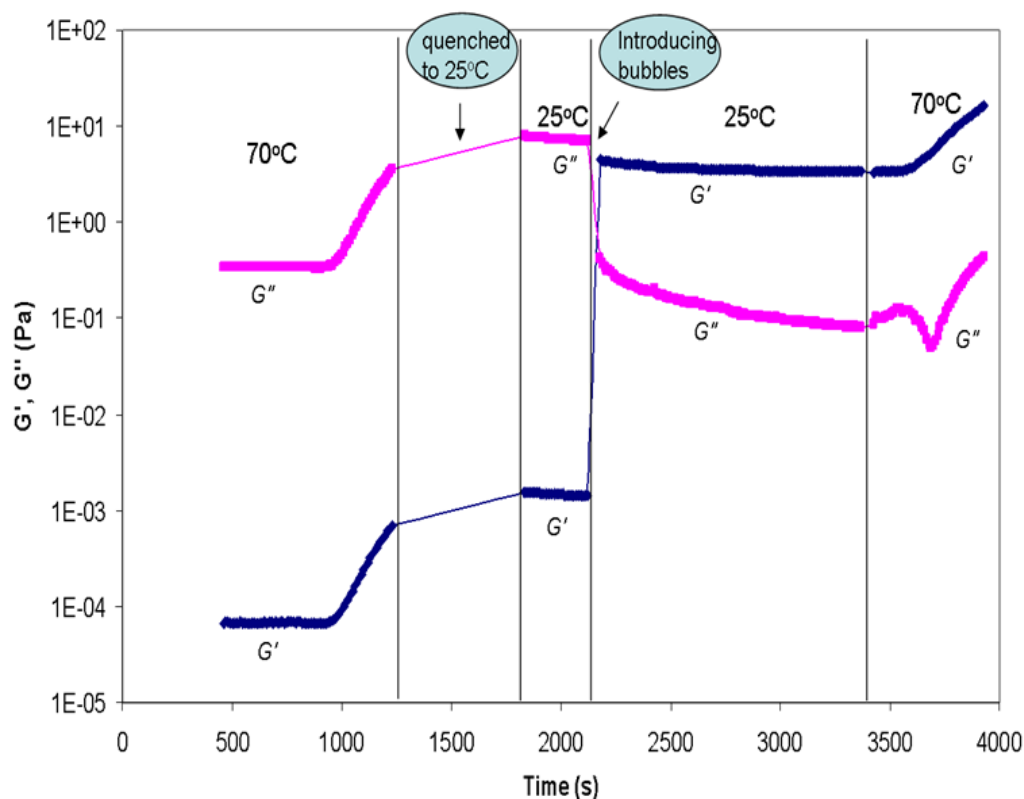


Figure 4.8 Effect of air bubbles on the rheological property change of a AZC solution (24000 ppm AZC in water at 70°C): case 2.

Absolute complex modulus

Due to the unusual sharp changes of the loss modulus and the storage modulus around the cross-over point, the cross-over point might not be accurate to represent the gel point. However, if the bubble effect is considered as an inherent part of interaction of the system, the crosslinking process can still be characterized by using a time sweep profile of complex modulus. In this study, the absolute value of complex modulus $|G^*|$ was calculated (Kavanagh & Ross-Murphy 1998) and chosen as a characteristic parameter to describe the gelation process (Zhong & Daubert 2004).

Figure 4.9a is a typical evolution profile of the absolute value of complex modulus for AZC self-crosslinking. The profile shows that the gelation process consists of three phases. Phase I represents an initial plateau, during which G' and G'' remain virtually constant, with G'' being much larger than G' (not shown in this figure), indicating that the polymer sample is a viscous liquid. This phase is also called the induction period (Prud'homme 1984). Normally, the induction time is the period prior to the gel point, during which crosslinking between polymer molecules can occur, but no global crosslinked network is formed yet. The induction period has been reported by many researchers for different polymers (Calvet, Wong et al. 2004; Sarvestani, He et al. 2007) and is generally dependent on crosslinker dosage, pH and temperatures (more detail will be discussed in the following sections). Following phase I, the complex modulus exhibits a period of rapid increase, referred to as the fast gelation phase (Phase II). In phase III, the increase rate of the complex modulus decreased, eventually reaching a plateau, indicating completion of the gelation process. Similarly, Sarvestani proposed three regions during the gelation of poly(lactide-co-ethylene oxide-co-fumarate) hydrogels (Sarvestani, He et al. 2007). Calvet studied the gelation of polyacrylamide and also defined three phases, and the data were fitted with a modified Hill equation (Calvet, Wong et al. 2004). The gelation of gelatin, on the other hand, has been divided into four phases (Normand, Muller et al. 2000). By analyzing the profiles of complex modulus, the kinetics of gelation can be quantified.

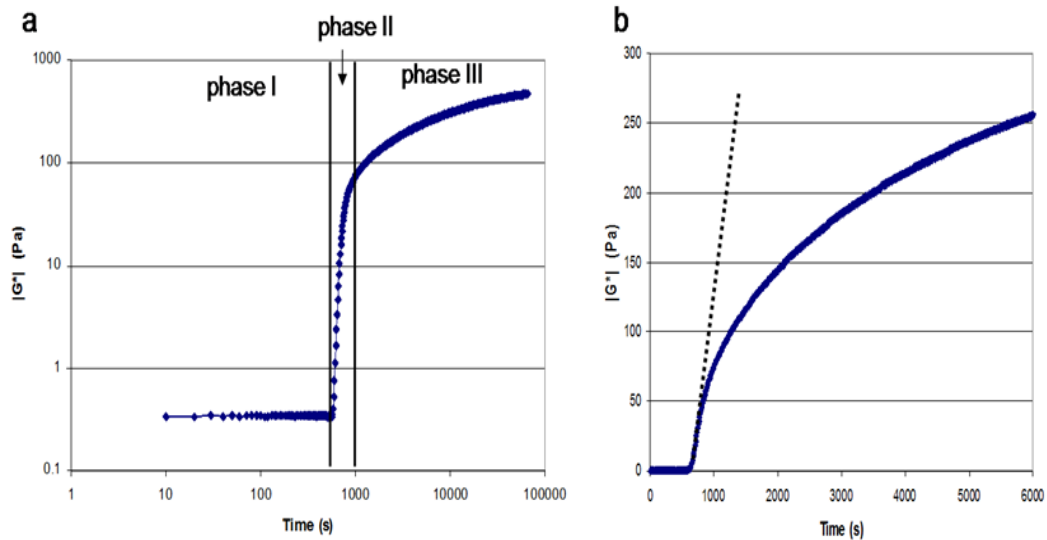


Figure 4.9 Typical profiles of the evolution of the complex modulus (a: 3 phase profile; b: profile with a tangent line) (6000 ppm AZC in water, 80°C, pH9)

4.3.3.3 AZC-starch co-crosslinking

The rheological changes for two-component blends of AZC and starch were characterized using the same methodology as for pure AZC solutions. The $|G^*|$ profiles in Figure 4.10 show a direct comparison between the pure solutions and the two-component solution for two different AZC concentrations. It can be seen that the two-component solution exhibits a faster initial increase of $|G^*|$ and a higher $|G^*|$ value after a given reaction time, which indicates a synergistic effect. This means that the development of the whole gel network is attributed not only to the self-crosslinking of AZC, but also to the co-crosslinking of AZC with starch.

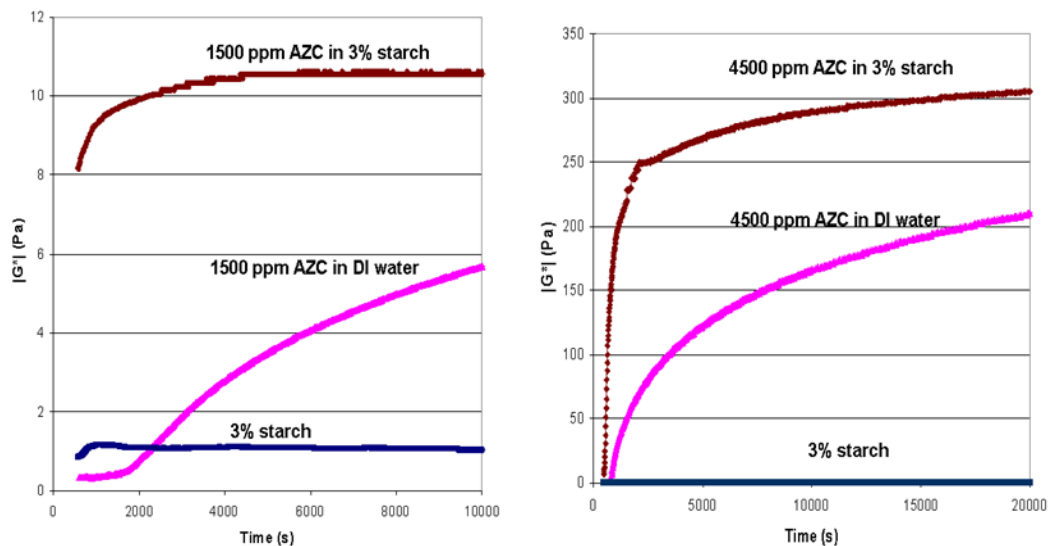


Figure 4.10 $|G^*|$ profiles for different reaction systems

4.3.4 Kinetic study of AZC self-crosslinking and AZC-starch co-crosslinking

To characterize the kinetics of gelation, modulus evolution curves have been analyzed by many researchers in various ways. In this study, we focus on the change of complex modulus. Equation 4.2 shows the link between the rate of bond formation du/dt and the rate of change of the complex modulus, $d|G^*|/dt$, which is the slope of complex modulus curve in the linear growth region (Omari 1994). For the gelation of polyacrylamide crosslinked by tri-valent chromium ions, Prud'homme measured the maximum rate of change of G' with respect to time, and considered it the maximum rate of crosslink formation (Prud'homme 1984). In Sarkar's study on kinetics of methylcellulose gelation, the fastest rate of increase in G' was used as a measure of the rate of gelation (Sarkar 1995). In this study, a similar method was applied, *i.e.* the maximum slope of the initial

increase of $|G^*|$ was determined (the dotted line in Figure 4.9b), and chosen to reflect the initial bond formation rate.

Normally, a plateau value of $|G^*|$ at long times can be used to represent the final strength of the network of interest. Figure 4.9a shows that after the initial rapid increase (phase II), the growth of $|G^*|$ indeed slows down, approaching a plateau. However, for lower AZC concentrations and lower reaction temperatures, the time needed for $|G^*|$ to reach a plateau was found to be extremely long. Under some conditions, a plateau could not be observed even after 20 hours. For most of our gelation studies, 5-6 hours was long enough to observe the viscoelastic property changes and longer observation times were not necessary.

4.3.4.1 Effect of AZC concentration for AZC self-crosslinking

For a single component system, the gelation/self-crosslinking process highly depends on the polymer concentration. In this study, the evolution profiles for AZC samples at different concentrations (600-6,000 ppm) were obtained (Figure 4.11). It can be seen that increasing the AZC concentration resulted in faster increase of $|G^*|$ at short times. The maximum slopes of the initial portions of the curves were determined, and are plotted in Figure 4.12, which show a good power-law scaling between $d|G^*|/dt$ and the AZC concentration, C_{AZC} :

$$d|G^*|/dt \sim (C_{AZC})^{3.0} \quad (4.6)$$

The power-law exponent of 3.0 for the kinetics of AZC self-crosslinking suggests that three AZC polymer chains participate in the formation of the primary junction zones. The C^3 power-law dependence of gelation rates was also reported in the literatures for other gelation systems. For example, a power-law of 2.7 was reported for the polyacrylamide-glyoxal gelation system (Omari 1994). It was also reported that the maximum gelation rate of methylcellulose (MC) following a power-law relationship for MC concentration with an exponent of 3.3 (Sarkar 1995).

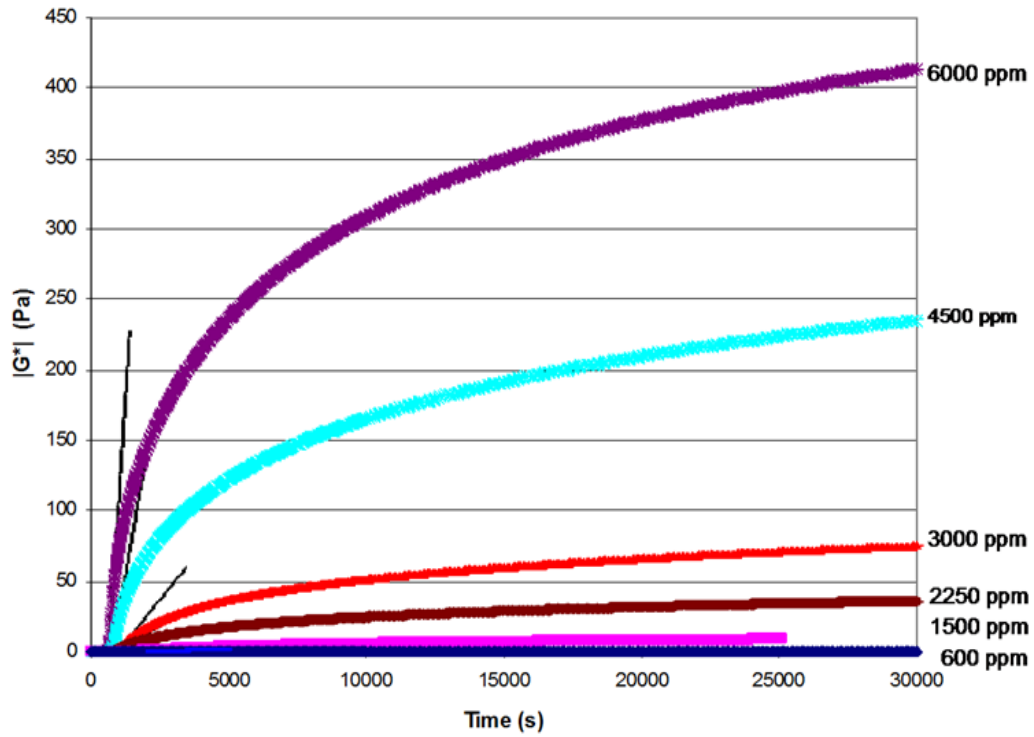


Figure 4.11 Profiles of $|G^*|$ for AZC self cross-linking at different AZC concentrations (the dotted lines represent the tangent at short times).

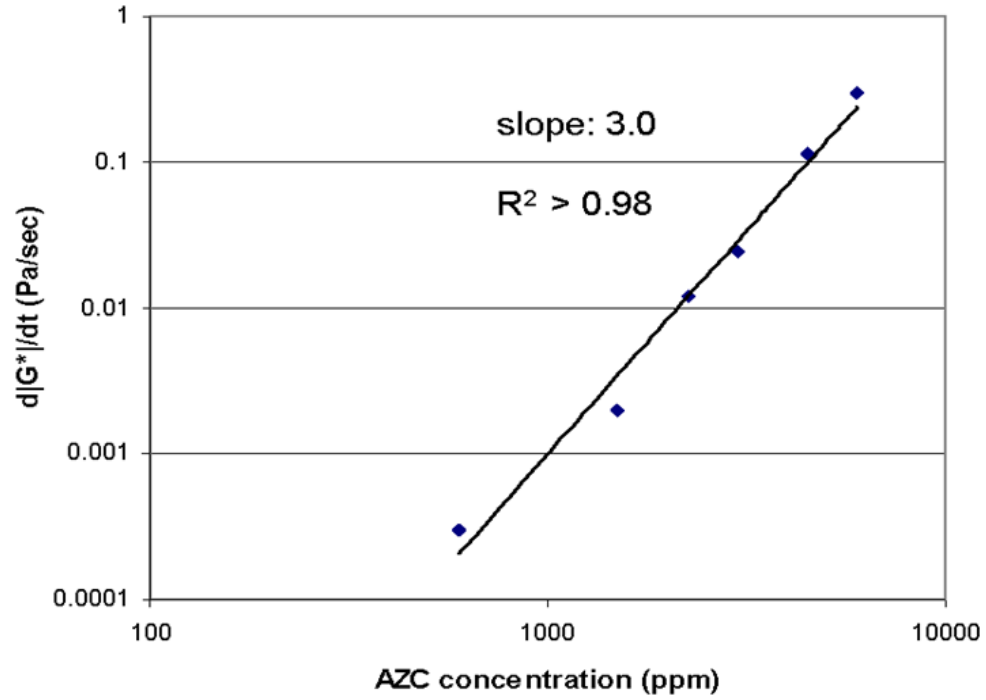


Figure 4.12 The initial rates of increase of $|G^*|$ for AZC self cross-linking at 80°C.

In addition, Figure 4.11 also shows that with increasing AZC concentrations, higher $|G^*|$ values were reached for the same reaction time. This is because at a higher AZC concentration, a more densely crosslinked network can be formed (Lin-Gibson, Walls et al. 2003). The values of $|G^*|$ at 20,000s are chosen and plotted with C_{AZC} (Figure 4.13). It can be seen that, the $|G^*|$ plot exhibits a good power law between the gel strength and AZC concentration:

$$|G^*|_{20000} \sim (C_{AZC})^{2.9} \quad (4.7)$$

The power-law scaling of modulus with concentration has been reported by many researchers with different values of the exponent n (2~3). Aguilera reported an exponent

close to 3.1 for whey protein isolate (Aguilera & Rojas 1997). Gaunet found that for some thermoreversible gels, the relationship between polymer modulus and concentration follows a power law with exponent 3 (Gaunet 1992). For the rest of this study, the value of $|G^*|$ at 20,000s, $|G^*|_{20000}$, was chosen to represent the ‘gel strength’. It should be noted that the gel strength at 20,000s only provides a snap shot of the gel network and not the actual ultimate gel strength. For the gelation at low temperatures, for example, the system at 20,000s had only reached the early stages of gelation (Nickerson, Patel et al. 2006).

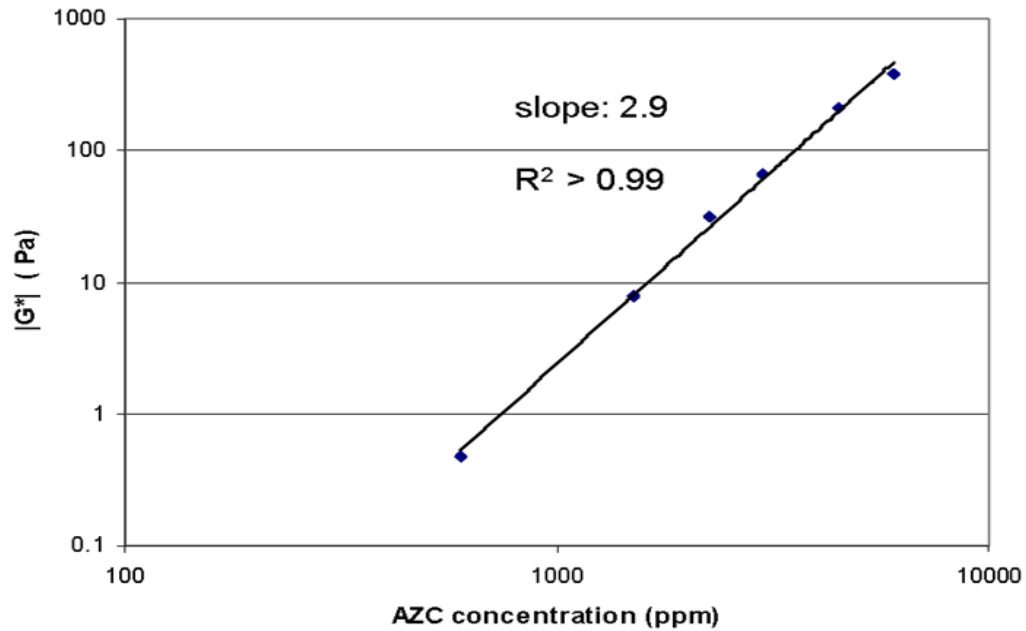


Figure 4.13 The values of $|G^*|$ at 20000s vs. AZC concentration for AZC self-crosslinking.

4.3.4.2 Effect of AZC concentrations on the gelation of AZC/starch blends

In the AZC-starch system, both starch-AZC crosslinking and AZC self-crosslinking can occur. Therefore, the amount of AZC in the mixture is expected to play an important role in the gelation process. From Figure 4.14, it can be seen that increasing the AZC concentration leads to faster increase of $|G^*|$, and higher values of $|G^*|$ after a fixed reaction time. This is expected because the crosslinking reaction rate depends on the reactant concentration.

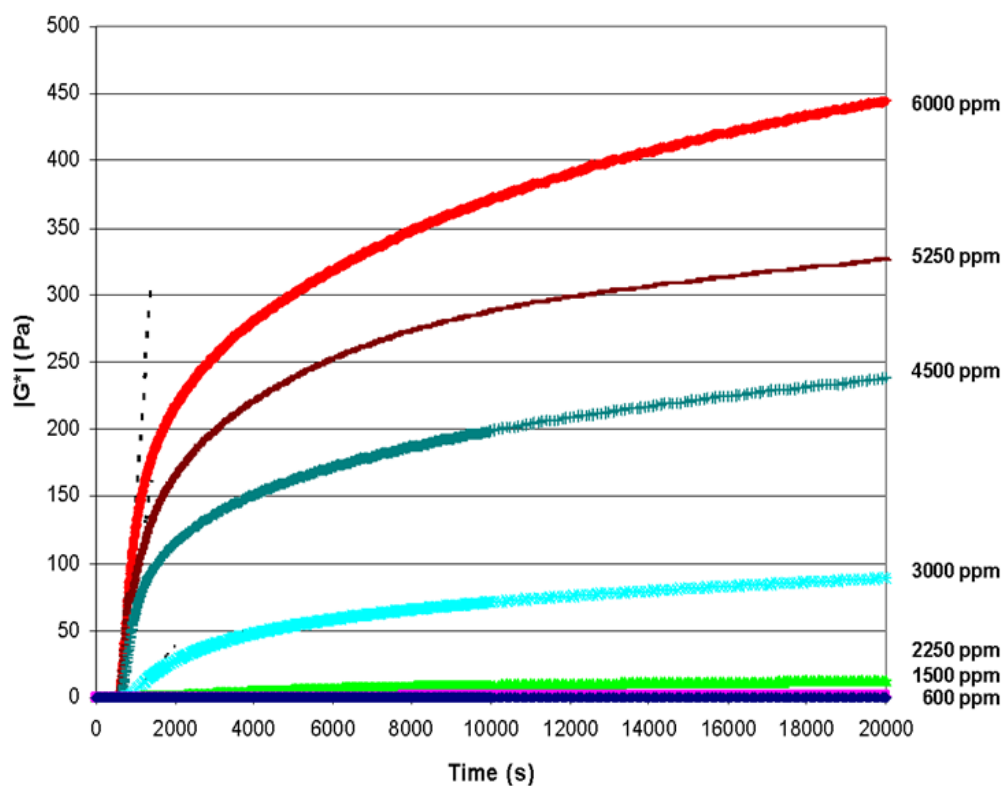


Figure 4.14 Effect of AZC concentration on gelation of AZC/starch blends (1% starch; 80°C; pH 9)

The dependence of the initial slopes (i.e. the initial gelation rate) on AZC concentration was determined, and it was found that the co-gelation of AZC and starch followed the power-law scaling of:

$$d|G^*|/dt \sim (C_{AZC})^{5.3} \quad (4.8)$$

The high power law (5.3) for the concentration dependence of the gelation rate is a surprising finding, which indicates the simple models (C^2 and C^3) are not applicable for the co-gelation of AZC and starch. Unlike the self-gelation of AZC which involves three AZC chains in the formation of junction zones, the AZC-starch junction zones might involve around 3 associated double helices according to Oakenfull's "domain model" (Ross-Murphy 1991). The high power law may be associated with higher-order aggregates of helices. In the process of co-gelation of AZC and starch, pre-aggregation and non-random co-operative process, such as nucleation and growth, might occur (Gosal & Ross-Murphy 2000). Although Oakenfull's explanation of high power laws has been challenged by other researches (Ross-Murphy 1991; Clark 1993), no other satisfactory explanation has been proposed so far. The high power laws (>4) for the dependence of gelation rates versus polymer concentrations were also reported in the literatures. Oakenfull and Scott found that the power law exponent n was 4.5 for *l*-carrageenan and 12.5 for *k*-carrageenan respectively (Oakengull & Scott 1986). The gel time reflecting the initial gelation rate was found to follow a C^6 concentration dependence for the gelation of maltodextrin aqueous solutions (Loret, Meunier et al. 2004).

Figure 4.14 also shows that the higher the AZC concentration, the higher the values of $|G^*|$ after a fixed reaction time. The dependence of the gel strength at 20,000s on AZC concentration was determined, and it was found that the power law exponent was 3.4, which is close to the widely reported third power law scaling.

$$|G^*|_{20000} \sim (C_{AZC})^{3.4} \quad (4.9)$$

4.3.4.3 Effect of starch concentrations on the gelation of AZC/starch blends

Besides the AZC concentration, the effect of starch concentrations on the gelation of AZC/starch blends was also studied. For a fixed amount of AZC, the initial reaction rate was found to depend on the amount of starch in the system. The higher the starch concentration, the more likely it is for an AZC molecule to react with starch. In Figure 4.15, a faster increase of $|G^*|$ for the systems with higher starch concentrations was observed. By plotting $d|G^*|/dt$ vs. starch concentration (not shown here), it was found that the maximum rate of $|G^*|$ change followed a power law relationship with starch concentration:

$$d|G^*|/dt \sim (C_{Starch})^{1.0} \quad (4.10)$$

The results indicate that the crosslinking of starch by AZC is a first order reaction. A similar result was reported by Omari who found that the gelation rate of scleroglucan (a polysaccharide) was dependent on the polymer concentration with a 1.4 power relationship (Omari 1995). For the hydroxypropylguar-titanium system, the exponent is 0.75. The

dependence of the gelation rate on polymer concentration was found to follow a power law with a coefficient of 1.25 for gelation of xanthan with trivalent metal ions (Nolte, John et al. 1992). However, the exponent is dependent on the structure and confirmation of the polymers. Normally, the values of the exponent for flexible polymers are much larger than that for rigid polymers, such as polysaccharides. An exponent value of 2.7 was reported for polyacrylamide (Prud'homme 1984).

Figure 4.15 also shows that $|G^*|$ (at 20,000s) increases with the increase of the starch concentration. This is because the more starch in the blends increased the probability of starch to AZC reaction. The $|G^*|_{20,000}$ vs. starch concentration also demonstrated a power law relationship:

$$|G^*|_{20000} \sim (C_{Starch})^{0.3} \quad (4.11)$$

The small exponent value of starch concentration indicates that the final strength of the crosslinked network is not highly dependent on the starch concentration.

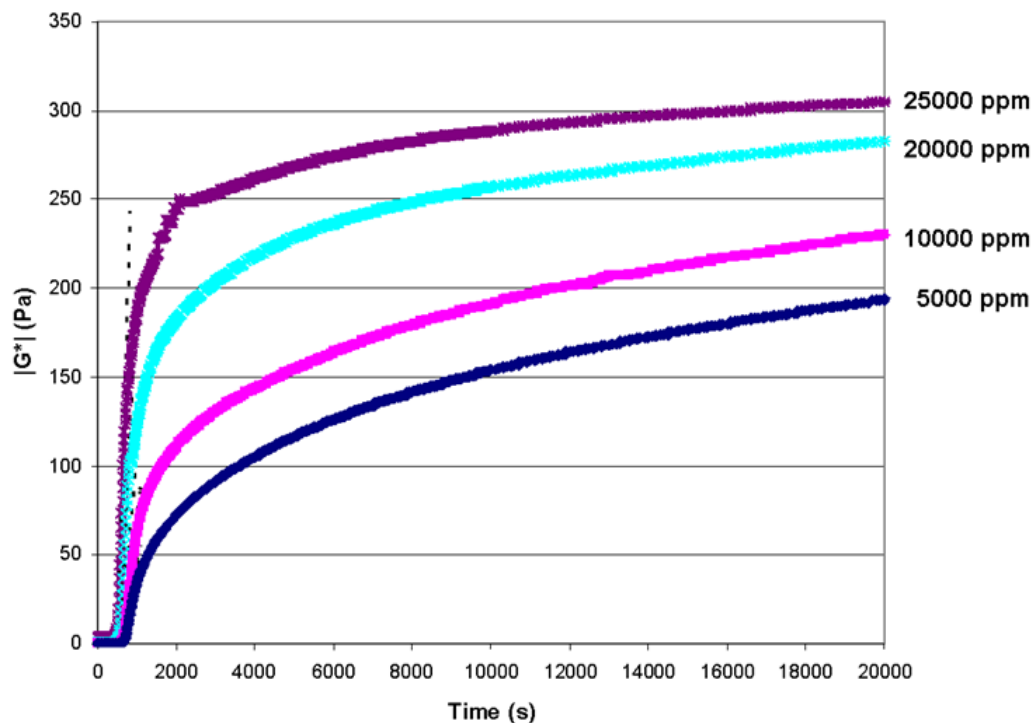


Figure 4.15 $|G^*|$ profiles at different starch concentrations for AZC-starch crosslinking.

The dependence of the initial bond formation rate (corresponding to $d|G^*|/dt$) and the gel strength at 20000s for both the pure AZC solutions and AZC-starch blends are summarized in Table 4.1. The results reveal different levels of significance of various parameters of the gelation process. AZC self-crosslinking is a third power process with respect to AZC concentration, both for the initial bond formation rate and the gel strength (at 20,000s). However, with an exponent of 5.3, the initial bond formation rate of AZC-starch blends has a much stronger dependence on AZC concentration than the pure AZC solutions. The efficiency of AZC as a crosslinking agent is strongly enhanced by the presence of starch molecules. Somewhat surprisingly, the starch concentration has a relatively less impact on the gelation rate. This may be because that starch is a rigid polymer with a much higher molecular weight than that of AZC, and no starch self-

gelation can occur in the system. Therefore, the smaller and more reactive AZC molecules demonstrate a dominate role during the co-gelation of AZC and starch.

Table 4.1: The dependence of the initial bond formation rate and the gel strength on different parameters

Crosslinking system	AZC solutions	AZC-starch blends	
	AZC concentration	AZC concentration	Starch concentration
$d G^* /dt$	$(C_{AZC})^{3.0}$	$(C_{AZC})^{5.3}$	$(C_{starch})^{1.0}$
$ G^* _{20000}$	$(C_{AZC})^{2.9}$	$(C_{AZC})^{3.4}$	$(C_{starch})^{0.3}$

For practical applications, the dosage of AZC should be minimized for saving the chemical cost. For example, in the case of fiber surface modification via starch grafting by using AZC as a crosslinking agent (more detail in chapter 5), more native starch with a lower cost rather than AZC should be grafted on fiber surface in order to improve the fiber-fiber bonding capability (Song, Zhao et al. 2009). However, the results shown in Table 4.1 indicate that the initial crosslinking rate and the gel strength are mainly attributed to the AZC concentration. The impact of starch contribution on the reaction kinetics is relatively less significant. That means there is only limited room for reducing the AZC dosage. The lower the dosage of AZC applied in the reaction system, the lower the gel strength of hydrogels. If the level of AZC is too low, a hydrogel might not be formed, and a large amount of starch grafting onto fibers might not be achieved.

4.3.4.4 Effect of reaction temperatures

For the crosslinking/gelation process, the temperature dependence of reaction rates can be described by an Arrhenius type equation 4.4 in which the rheological parameter change rate dG/dt is used to express the reaction rate (Ahmed, Ramaswamy et al. 2008). The logarithmic form of equation 4.4 can be written as:

$$\ln(dG/dt) = \ln(A) - E_a/RT \quad (4.12)$$

Therefore, by plotting $\ln(dG/dt)$ vs. $1/T$, the activation energy E_a can be determined from the slope if a linear relationship exists.

In this study, the isothermal gelation of AZC solutions and AZC-starch blends was conducted over a temperature range of 50-90°C. Figure 4.16 presents the $|G^*|$ profiles for different reaction temperatures. It was found that the induction period became significantly shorter with the increase of temperatures. For AZC self-crosslinking (Figure 4.16 left) at 90°C, the induction time is only 600s, while it is around 4800s at 70°C. A similar result was reported for the gelation of polyacrylamide (Calvet, Wong et al. 2004).

For the both reaction systems, the initial bond formation rate ($d|G^*|/dt$) and the gel strength at 20000s are highly dependent on temperatures. Figure 4.16 shows that the higher the temperature, the faster $|G^*|$ increase, and the larger the value of $|G^*|$ at a similar time.

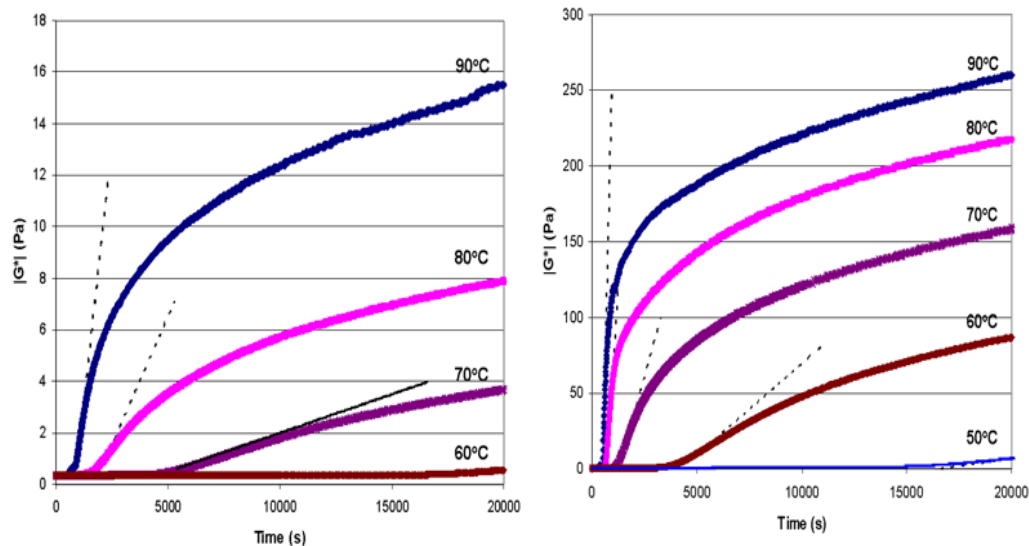


Figure 4.16 Effect of temperatures on the gelation process (left: AZC 1500ppm in water; right: AZC 4500 ppm in 1% starch)

The maximum slopes of the initial increase portion of the curves at different temperatures were determined, and summarized in Table 4.2. By plotting $\ln(d|G^*|/dt)$ vs. $1/T$, the Arrhenius plots were obtained (Figure 4.17). It can be seen that, for both AZC self-crosslinking (the solid lines) and AZC-starch co-crosslinking (the dash line), the plots exhibit a good linearity. By using the slopes of the lines (i.e. $-E_a/R$), the activation energy values were calculated. For the system of AZC self-crosslinking at different AZC concentrations (1500 ppm and 6000 ppm), the activation energy values are 145 ± 9 kJ/mol and 151 ± 4 kJ/mol respectively. According to the collision theory of reaction rates, the activation energy is the energy barrier for the reaction of individual molecules. Therefore, theoretically, the activation energy is independent of polymer concentrations. However, the Arrhenius equation is an empirical equation. The parameter used here, the complex modulus is a macro description of polymer network. Therefore, slight difference of the activation energy values obtained for the systems with different concentrations is

possible. The activation energy of AZC-starch co-crosslinking determined from the plot in Figure 4.17, is 139 ± 5 kJ/mol which is slightly lower than that of AZC self-crosslinking. This means that the energy barrier of the reaction between AZC and starch molecule is close to that of the reaction between AZC and AZC molecules. Therefore, from the point of molecule reactions, the preference of AZC to AZC and AZC to starch is comparable. In addition, the values of activation energy obtained are of the same order as those of starch or other polysaccharide gelation which are within the range of 30-138 kJ/mol (Omari 1995; Pielichowski, Tomasik et al. 1998; Ahmed, Ramaswamy et al. 2008).

Table 4.2 The initial change rates of complex modulus (absolute value) and the activation energy values for different reaction systems.

System	d G* /dt					Activation Energy (kJ/mol)
	50 °C	60 °C	70 °C	80 °C	90 °C	
1500 ppm AZC in water	/	0.0001	0.0003	0.002	0.008	145.0
6000 ppm AZC in water	/	0.015	0.060	0.30	1.07	151.1
4500 ppm AZC in 1% starch	0.002	0.012	0.05	0.21	0.59	139.3

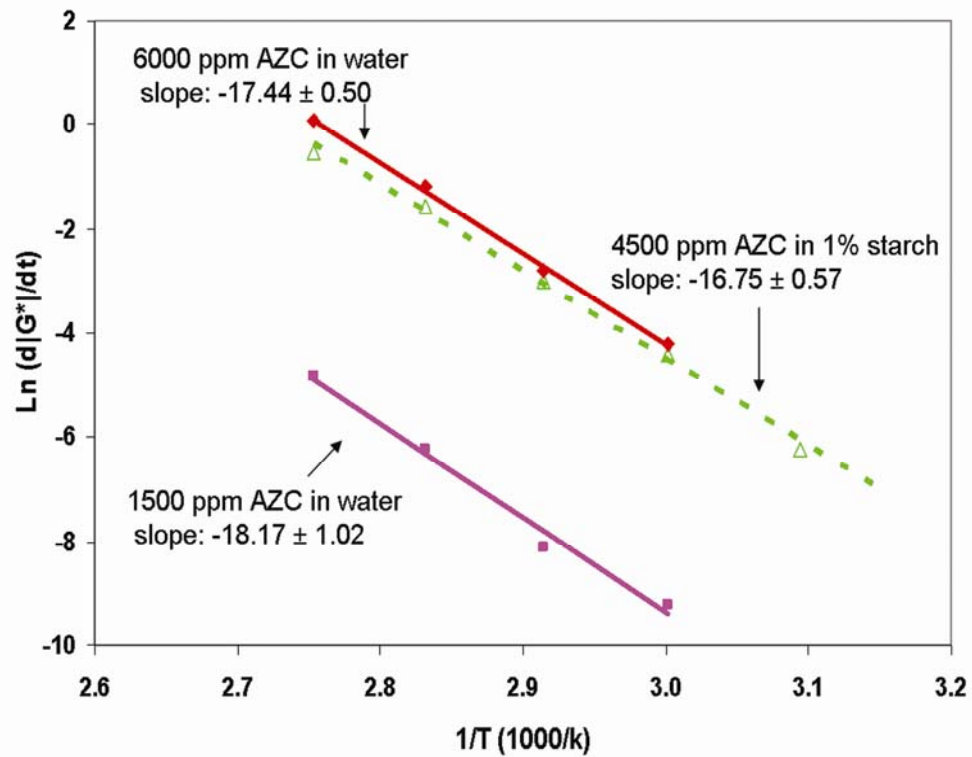


Figure 4.17 The Arrhenius plots of the initial $d|G^*|/dt$ on isothermal gelation of AZC solutions and AZC/starch blends

4.3.4.5 Effect of solution pH

The chemistry of AZC is very sensitive to the solution pH (Omari 1995). It was reported that the active pH range of AZC is 6-10. The crosslinking studies were conducted at different pH values. Figure 4.18 shows that the induction time is shorter at the lower pH values. This is because at low pH, AZC is not stable and the self-decomposition occurs (forming crystalline metal), which might trigger crosslinking. It was also found that increasing pH value led to higher gel strengths i.e. the values of $|G^*|$ at 20,000s in Figure 4.18 (with an exception of pH 10). Omari also reported that the gel formation could be enhanced by increasing pH for the scleroglucan-zirconium system (Omari 1995). The low

gel strength at pH 10 is likely caused by zirconium hydrolysis which was enhanced in alkaline media. With respect to the final gel strength, pH 9 is the optimal reaction condition, which agrees well with the results from our previous publication (Song, Zhao et al. 2009). A similar result was obtained for the effect of pH on the starch-AZC co-crosslinking.

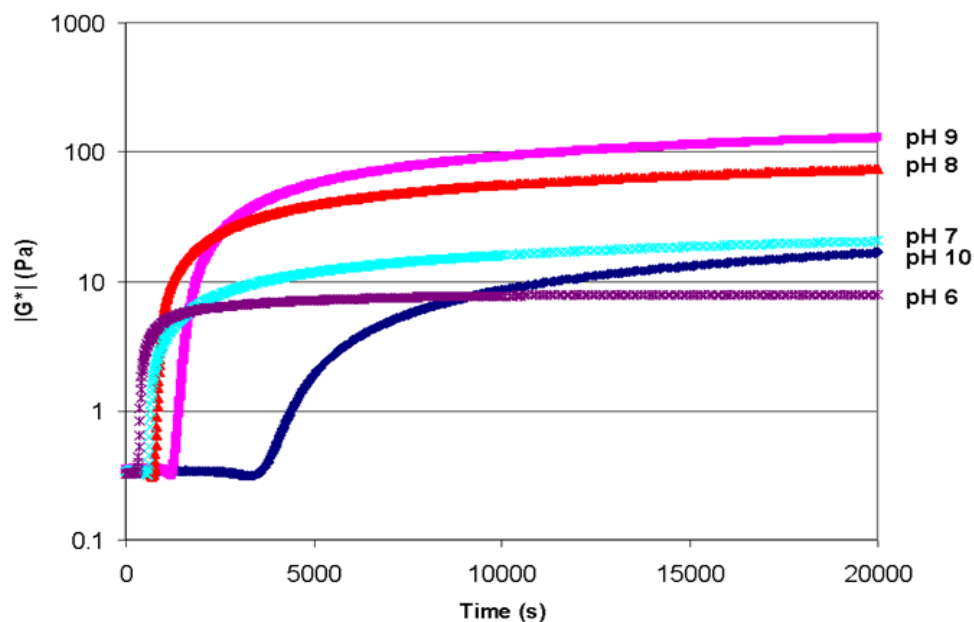


Figure 4.18 The effect of solution pH on AZC self-crosslinking (4500 ppm AZC in water, 70°C)

4.3.5 Comparison of reaction rates in different reaction systems

The initial change rates of absolute complex modulus for AZC self-crosslinking and AZC-starch co-crosslinking are compared, and illustrated in Figure 4.19. It can be seen that the values of $d|G^*|/dt$ for AZC-starch co-crosslinking is larger than those for AZC self-crosslinking, regardless the dosage of AZC, which may be due to that AZC-starch

co-crosslinking has a lower energy barrier (activation energy) than AZC self-crosslinking.

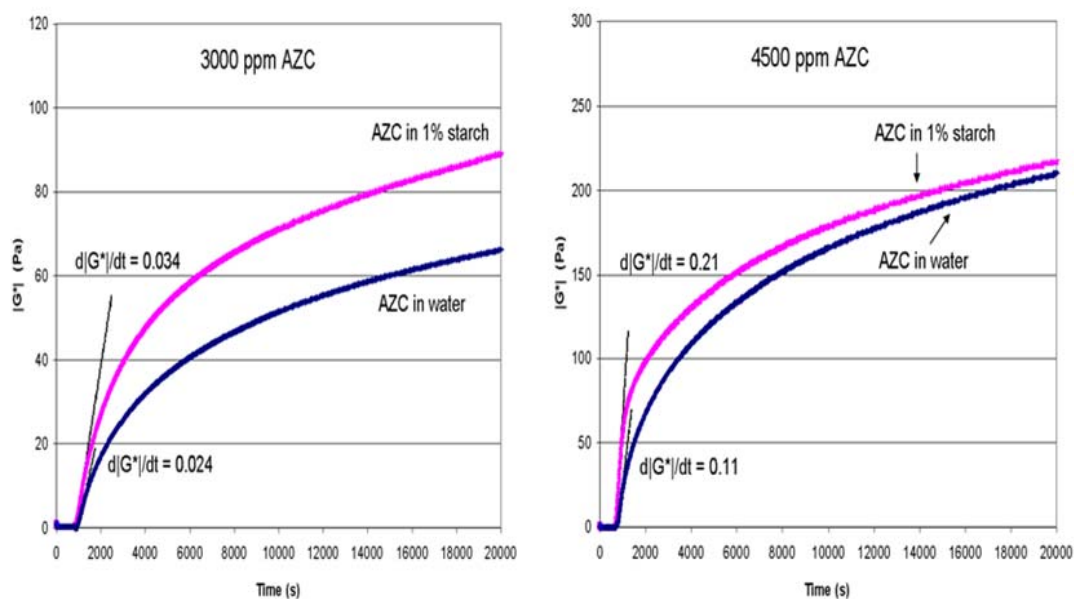


Figure 4.19 $|G^*|$ profiles for different reaction systems (80°C)

The mechanism of the AZC reaction with polymers containing hydroxyl group (Figure 2.7) shows that CO_2 is generated when AZC reacts with starch or with itself. The release rate of CO_2 should be proportional to the rate of link formation. In this study, GC headspace multiple sampling was used to monitor the release of CO_2 over the reaction time. Figure 4.20 represents the CO_2 release curves for two different cross-linking systems. It can be seen that AZC self-crosslinking in water and AZC-starch co-crosslinking in the blend system have a similar CO_2 release rate, which means AZC self-crosslinking and AZC-starch co-crosslinking have a similar link formation rate. The reaction preference of AZC with AZC and the reaction preference of AZC with starch are comparable.

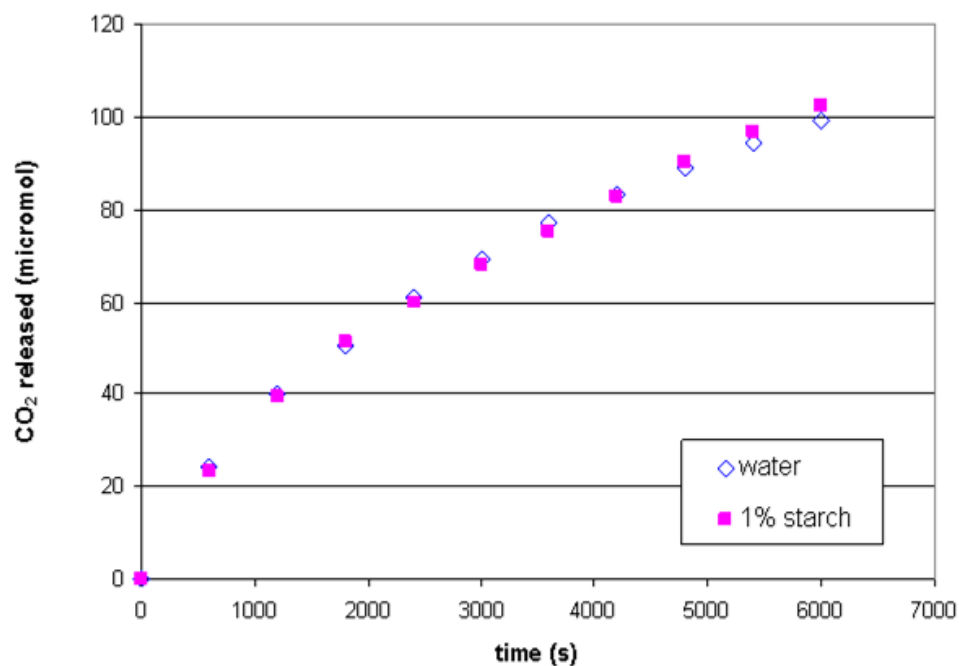


Figure 4.20 The release of CO₂ over time for different reaction systems (3000ppm AZC in water and in 1% starch at 80°C)

Please note that CO₂ release rate reflects the reaction rate between molecules. At an elevated temperature, the reaction can occur immediately after the addition of AZC in the water or starch shown in Figure 4.20. The initial generated links between molecules are not enough to form a gel in the system. That is why an induction period where the values of $|G^*|$ kept constant was observed in the profile of $|G^*|$ evolution (Figure 4.9). As a macro level characterization, the rate of $|G^*|$ change, $d|G^*|/dt$ represents the development of crosslinked hydrogel network, i.e. reflecting the rate of crosslinks formation to some extent. The above result indicates that the gel network development shows some delay following the link formation, *i.e.* CO₂ release.

4.4 Conclusions

In this chapter, the evolution of complex modulus (absolute value) for the AZC solutions and the AZC-starch blends was characterized. The kinetics of the crosslinking processes (the gelation) for the two systems were determined. It was found that the dependence of both the initial bond formation rate and the gel strength exhibit a power law scaling with both AZC and starch concentrations. The development of the crosslinking network is highly dependent on the AZC concentration. The effect of starch concentration on the gelation rate is relatively less significant for AZC-starch mixture solution. The temperature dependence of the crosslinking rate depicted in the Arrhenius plots shows a good linearity. The activation energy of AZC self-crosslinking is approximately 145-151 kJ/mol, while the activation energy of AZC-starch co-crosslinking is 139 kJ/mol. The CO₂ release rates show that AZC self-crosslinking and AZC-starch co-crosslinking have a similar reaction (i.e. link formation) rate. The reaction preference of AZC with AZC and the reaction preference of AZC with starch are comparable. Furthermore, the gel network development shows some delay following the link formation, *i.e.* CO₂ release.

CHAPTER 5

SURFACE MODIFICATION OF CELLULOSE FIBERS BY STARCH GRAFTING WITH CROSSLINKERS*

Abstract

In this chapter, a facile method to graft biodegradable starch onto fiber surfaces through the hydrogen bond formation among cellulose, starch and ammonium zirconium (IV) carbonate (AZC) was developed. The effects of grafting conditions, including pH, temperature, fiber consistency, crosslinker, starch dosage and mechanical agitation on the grafting yield were systematically investigated. Optical and electron microscopes clearly revealed that, after grafting, the fiber surface was covered by a hydrogel of starch. A significant improvement of the water retention value (WRV) of fibers with starch grafting was also demonstrated.

* The contents in this chapter are based on the research described in the following publication:

Song, D., Zhao, Y., Dong, C. and Deng, Y., *Surface modification of cellulose fibers by starch grafting with crosslinkers*. Journal of Applied Polymer Science 2009. 113(5): 3019-3026.

5.1 Introduction

Cellulose fibers have been widely used in various applications. In order to create or enhance some desired properties, physical, physico-chemical, or chemical treatments are normally conducted on fibers. The chemical methods for fiber modification mainly include fiber wall crosslinking (Stamm 1959; Zhou, Luner et al. 1995), layer-by-layer (LbL) nanocoating technology (Zheng, McDonald et al. 2006; Lvov, Grozdits et al. 2007) and grafting of polymers onto fibers (Kamdem, Riedl et al. 1991; Gupta, Sahoo et al. 2002; Loría-Bastarrachea, Carrillo-Escalante et al. 2002; Abu-Ilaiwi, Ahmad et al. 2004; Belgacem & Gandini 2005; Coskun, Mür et al. 2005; Fan, Zhao et al. 2006; Pulat & Isakoca 2006; Guan, Xiao et al. 2007; Jain, Xiao et al. 2007). However, for most of the above methods, there are some drawbacks such as complex and rigorous reaction conditions, long reaction time, high cost of chemicals and environmental concerns (Roche 2006).

Directly grafting commercial available polymers onto cellulose fibers by simply adsorption or layer by layer self-assembly has been reported (Roche 2006). For example, cationic polymers can be physically grafted onto fiber surface via electrostatic adsorption, because cellulose fibers have a negative surface charge. Although the simple adsorption method can physically graft polymer on fibers, the maximum adsorption amount is limited by the saturation of adsorption. The low amount of polymer grafting sometimes cannot satisfy certain applications. For example, grafting of superabsorbent on wood fibers is a technique that has been widely used in the diaper industry. For such

applications, large amount of polymers need to be grafted on fiber surface. On the other hand, anionic or non-ionic polymers may be chemically grafted onto cellulose fibers by using appropriate crosslinkers or couple agents.

In Chapter 4, the mechanism and kinetics of AZC-starch crosslinking were investigated, and it was found that starch hydrogel could be formed using AZC as a crosslinker. According to the mechanism of reaction proposed by Farnworth (Farnworth, Jones et al. 1981) (Figure 2.8), AZC can also react with cellulose by forming hydrogen bonds. One benefit of using AZC as a crosslinker is that the crosslinking reaction with cellulose and starch can occur in water and no high temperature drying-curing is required though heat can speed the crosslinking process.

In this chapter, a simple technique using AZC as a crossliker or coupling agent to graft raw starch on cellulose fibers was developed. The effects of grafting conditions, such as pH, temperature, fiber consistency, crosslinker and starch dosages, on grafting yields were systematically investigated. The morphology of starch grafted fiber was revealed by optical microscope and SEM images. The bonding strength of the starch hydrogel on the fiber surface was studied by applying different shear forces. The water retention value (WRV) of modified fibers was also evaluated.

5.2 Experiments

5.2.1 Materials

Commercial pulp (bleached softwood kraft pulp) with an initial Canadian standard freeness (CSF) of 750 ml was received from Georgia Pacific, USA. The raw corn starch (B200) was provided by Grain Process (Muscatine, Iowa USA). The starch was cooked for 40 minutes using a rotary evaporator at 95°C. Ammonium zirconium (IV) carbonate solution (contains 1-2% tartaric acid as stabilizer) was purchased from Aldrich, USA.

5.2.2 Methods

Fiber modification procedure

The basic process of grafting was to add AZC crosslinker into fiber slurry to react with fibers for a few minutes, followed by addition of precooked starch. In order to accurately determine the grafted amount of starch on fibers, the wood fines in the pulp was pre-removed using a Bauer-McNett Fiber Classifier, and only the long fibers retained on 150 mesh wire was collected and used.

The starch grafting process is demonstrated in Figure 5.1. Certain amount of fiber (2g o.d. weight in this study) was put into a 300 ml glass beaker, and appropriate amount of deionized water was added to prepare fiber slurry at a designed consistency (1-4%). Then fiber was soaked at least 2 hours and well dispersed in water with mechanical

stirring before use. The beaker was put in a water bath at 80°C or a higher temperature, and a moderate mechanical stirring was applied by using a food mixer at 200 rpm. The required amount of AZC solution was slowly added into the fiber slurry, and the pH of the fiber slurry was adjusted by using 5% NaOH or 5% HCl. After mixing for 2-3 minutes, the required amount of precooked starch solution was added slowly into the fiber slurry. After reaction for 5 minutes, the beaker was cooled with cold water to stop the grafting reaction.

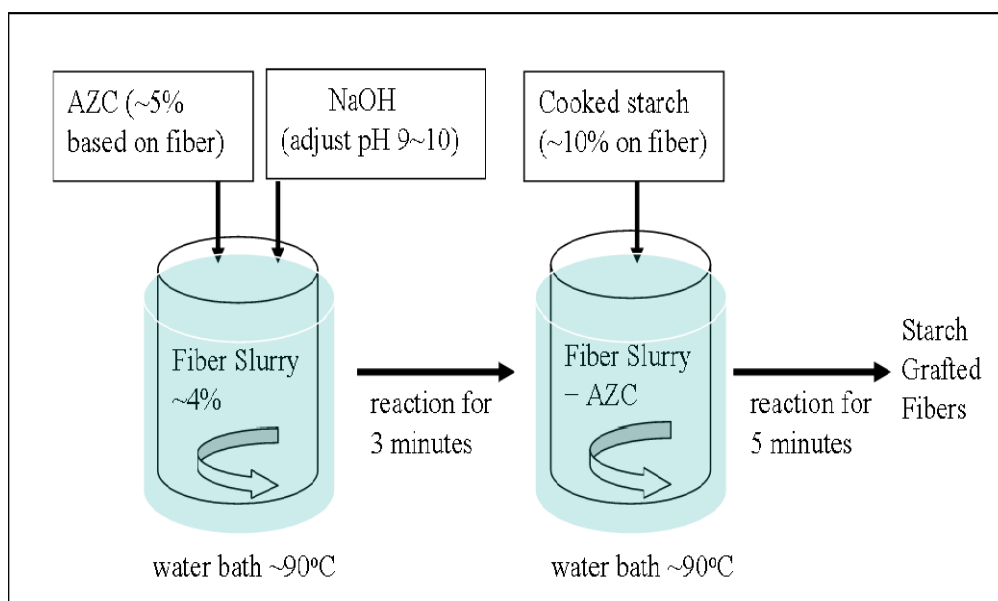


Figure 5.1 A schematic process of AZC-starch grafting treatment.

Amount of grafting and grafting yield determination

The starch-grafted fiber sample was thoroughly washed with a large amount of water (about 4 liter water for 2 g oven dried fiber) by using a dynamic drainage jar with a 200

mesh screen under moderate agitation at 400 rpm, aiming to remove the ungrafted starch. The samples collected on the screen were transferred to a pre-weighted filter paper and dried in 105°C. Then the amount of grafting on fibers and grafting yield were determined by using the following equations:

$$\text{Amount of Grafting (\%)} = \frac{\text{Mass of Grafted Fiber} - \text{Mass of AZC} - \text{Mass of Initial Fiber}}{\text{Mass of Initial Fiber}} \times 100 \quad (5.1)$$

$$\text{Grafting Yield (\%)} = \frac{\text{Mass of Grafted Fiber} - \text{Mass of AZC} - \text{Mass of Initial Fiber}}{\text{Mass of Starch Added}} \times 100 \quad (5.2)$$

Morphology of fiber surface

Optical microscope and scanning electron microscope (Hitachi S-800 FE-SEM) images were taken to reveal the morphology of fiber surface.

Water retention value (WRV) test

The water retention value (WRV) of fiber was determined according to TAPPI UM 256. Fiber samples (0.5 g oven dried) were diluted to a consistency of 0.2%, and then drained onto a fine mesh screen at the bottom of a centrifuge cup. The samples in the centrifuge cups were centrifuged at 900G's for 30 minutes. The obtained fiber pad was weighted and dried in an oven at 105°C for 3 hours. After drying, the mass of fiber samples was

determined. The water retention value (WRV) was defined as the ratio of water mass in the wet fiber pad after centrifuging to the oven dried mass of fiber.

5.3 Results and Discussion

5.3.1 Morphology of modified fibers

As AZC can directly form chemical or hydrogen bonds with the hydroxyl groups on cellulose, it is expected that an AZC layer can form on fiber surface by mixing it with fibers at desired temperature and pH. However, because of the multi-reactive sites of an AZC polymer chain, there must be some unreacted sites on the AZC polymer chains. When starch is added, unreacted sites of AZC will further react with hydroxyl groups of starch via hydrogen bonding. As a result, starch could be grafted onto the fiber surface through the bridging of AZC. Moles (Moles 1992) proposed a similar process to use zirconium-based coupling agents as adhesion promoters in ink industry.

Figure 5.2 is a comparison of unmodified fibers and starch-grafted fibers. The fibers in the left beaker are unmodified fibers dispersed in water. After starch grafting treatment, the wood fibers formed large flocs due to the grafted starch hydrogel, and left a clear water layer on the top (the right beaker in Figure 5.2). Generally speaking, the more the starch added, the bigger the flocs were formed. The optical microscope pictures (Figure 5.3 a, b) illustrate a remarkable change of fiber surface before and after starch grafting. It can be seen that the fiber surface (Figure 5.3 b) was covered by large amount of starch

aggregates and “starch fibrils” after starch grafting. It is believed that with such “starch fibrils”, the water retention value and the bonding capability of fiber would be significantly improved.



Figure 5.2 Comparison of fiber slurry before (left) and after (right) starch grafting.

The SEM pictures of unmodified fibers and starch grafted fibers were also taken in this study (Figure 5.3 c, d). More clear change of morphology of fiber surface before and after starch grafting can be clearly seen. Compared with the unmodified fibers, the surface of grafted fibers became rougher. Furthermore, both the optical microscope pictures and SEM images indicate that the grafted starch was not uniformly distributed but formed some aggregates on fiber surface, resulting in the increase of roughness of fiber surface. The morphology change of fiber is different from that by simple polymer adsorption, such as cationic starch and cationic polyacrylamide, in which the fiber is covered only by a thin film of polymer and no significant aggregates or fibrils can be observed (Roche 2006).

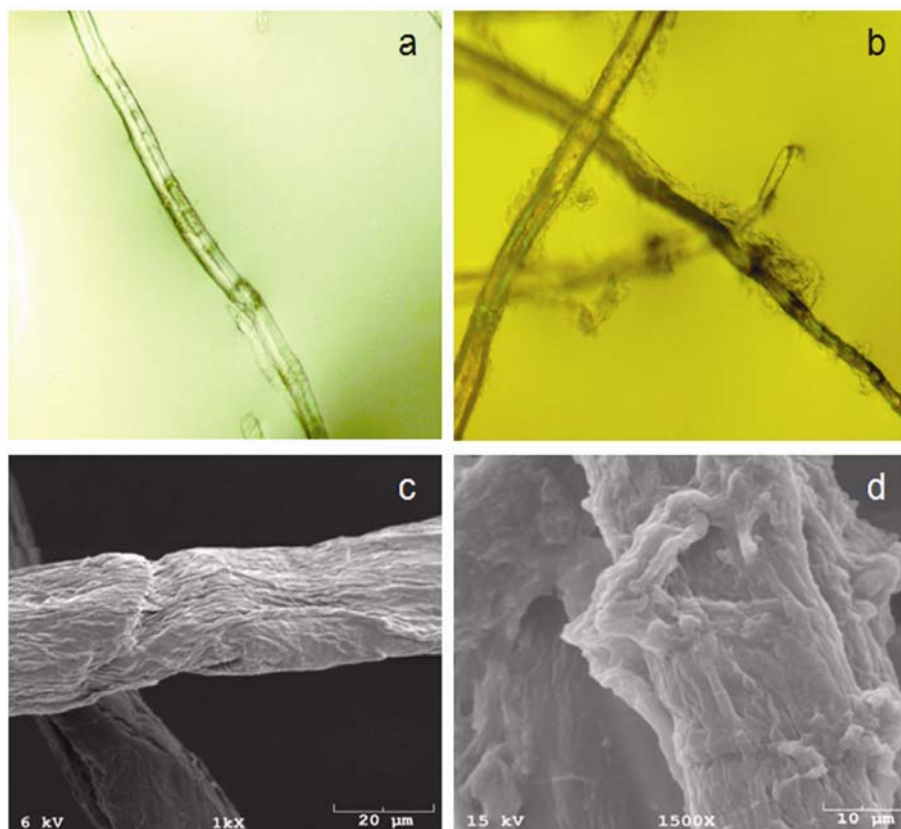


Figure 5.3 Microscope pictures of fibers: a. optical microscope picture of unmodified fibers; b. optical microscope picture of starch grafted fibers; c. SEM picture of unmodified fibers; d. SEM picture of starch grafted fibers.

5.3.2 Effects of grafting conditions on grafting yields

There are several possible crosslinking reactions, such as fiber-AZC-starch, fiber-AZC-fiber, and starch-AZC-starch interaction in the system studied here. As a crosslinker, AZC would have different reactivity at different reaction conditions, such as pH, temperatures, fiber consistency, AZC dosage, stirring speed. Consequently, the grafting performance would be highly dependent on these conditions.

The grafting yield at different pH was determined and illustrated in Figure 5.4. It can be seen that the grafting yield increased up to pH of 9, and then decreased with further increase of pH. The low grafting yield at low pH is mainly attributed to the decomposition of AZC at acid conditions (Floyd & Boss 1995). Wolff et al. reported that the active pH range of AZC in surface sizing is around 5.5-10 (Wolff, Calcar et al. 1996).

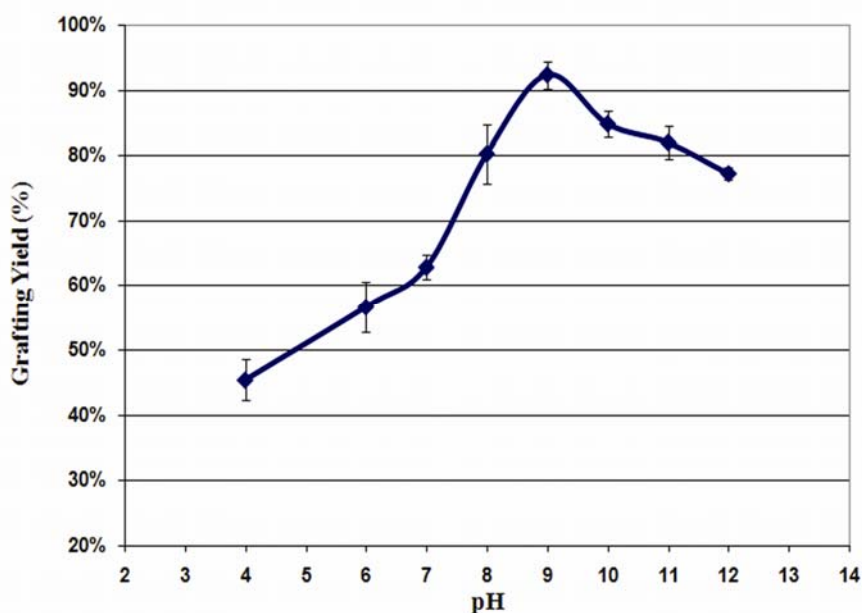


Figure 5.4 Effect of pH on grafting yield (fiber consistency: 3%; starch dosage: 10% based on fiber; AZC: starch = 1:2; temperature: 95°C).

As shown in the starch rheological measurement (chapter 4), the crosslinking process can be speeded up by increasing the reaction temperature. It is likely that the fast reaction rate may also result in a high grafting degree of starch on fibers. In this study, the grafting yield at different temperatures for a fixed reaction time (5 minutes) was investigated. Figure 5.5 indicates that, the higher the reaction temperature, the higher the grafting yield. One of the reasons for the high grafting yield is probably due to the fast dehydration at a high temperature and more bond formation, resulting in the shrinking of

starch hydrogel to form a hard gel which can bond to fiber surface stronger than the soft gel formed at a low temperature. From the reaction between AZC and starch (Figure 4.16) at 90°C, it took more than 5 hours to accomplish the crosslinking reaction. In this part of study, 80-90% of grafting yield could be achieved only after 5 minutes. Theoretically, a higher grafting yield, and even 100% yield could be achieved if more reaction time was chosen.

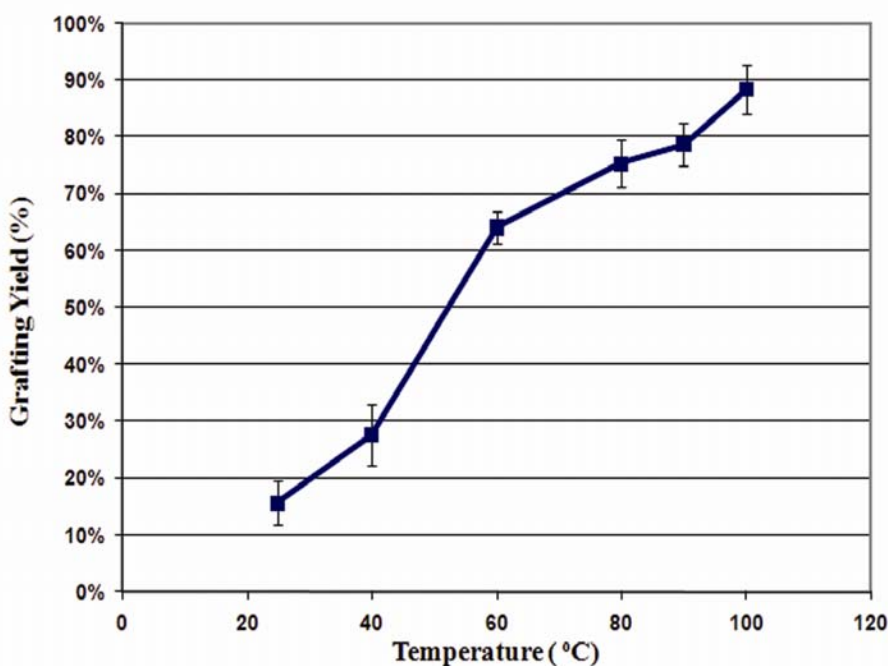


Figure 5.5 Effect of temperature on grafting yields (pH: 9; fiber consistency: 3%; starch dosage: 10% based on fiber; AZC: starch = 1:2).

Fiber consistency is also an important parameter for the grafting reaction system. It can be seen from Figure 5.6 that there is an optimal fiber consistency, i.e. at around 3%. At a lower fiber consistency, fibers could not provide enough surface area for AZC and starch to graft on fiber surface so that large amount of starch would form homo-crosslinked hydrogel particles. However, when fiber consistency was too high (higher than 3%), the

fibers formed large fiber flocs and could not be well dispersed in water. The poor mixing of the system at a high fiber consistency might end up with some unreacted AZC or starch, resulting in a low grafting yield.

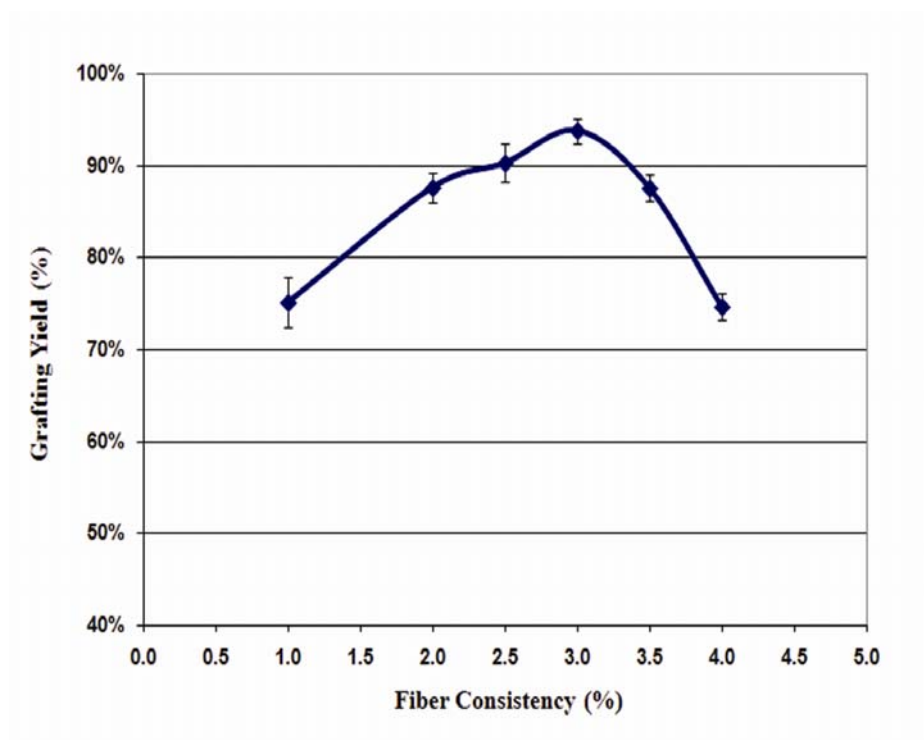


Figure 5.6 Effect of fiber consistency on grafting yield (pH: 9; starch dosage: 10% based on fiber; AZC: starch = 1:2; temperature: 95°C).

It is expected that AZC functions as a crosslinker or a coupling agent between cellulose fibers and starch during the reaction. Figure 5.7 shows that, at a starch to fiber ratio of 0.05 to 1, the grafting yield first increased with AZC dosages and then leveled off at AZC dosage of ~3% based on fibers. At this condition, the grafting yield reached ~98%. When 10% starch was used, the grafting yield was also increased with the AZC dosage. However, after reaching a peak value, the grafting yield decreased when more AZC was added. The reason for the decrease of the grafting yield at the high AZC dosage is the formation of homo-crosslinked starch gel. It can be concluded that, from both a high

grafting yield and a low cost point of view, too high AZC to starch ratio should be avoided in a practical application.

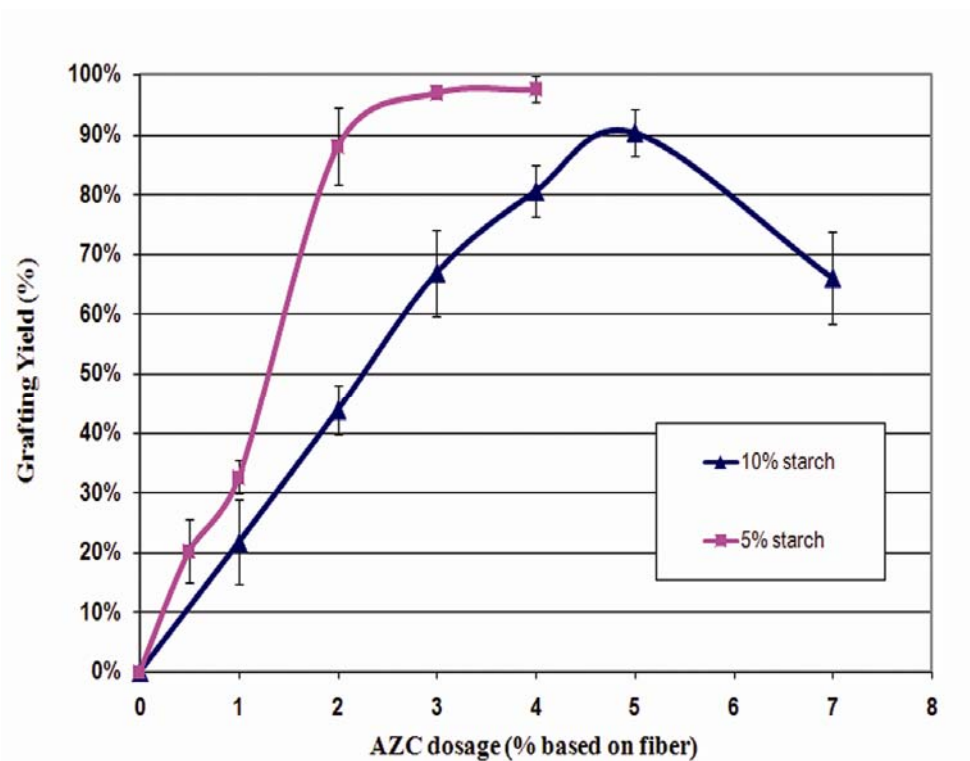


Figure 5.7 Effect of crosslinker dosage on grafting yield (pH: 9; fiber consistency: 3%; Temperature: 95°C).

The effect of starch dosage on the grafting performance was also determined (Figure 5.8). The results indicate that the more starch added, the higher the amount of starch grafted on fibers. However, the grafting yield, i.e. starch retention rate, was decreased with the increase of starch dosage, suggesting more un-grafted portion of starch in the system. It can also be seen that a highest grafting yield could be achieved at 5% starch addition level at current grafting condition (i.e. pH 9, temperature 95°C, AZC:starch = 1:2).

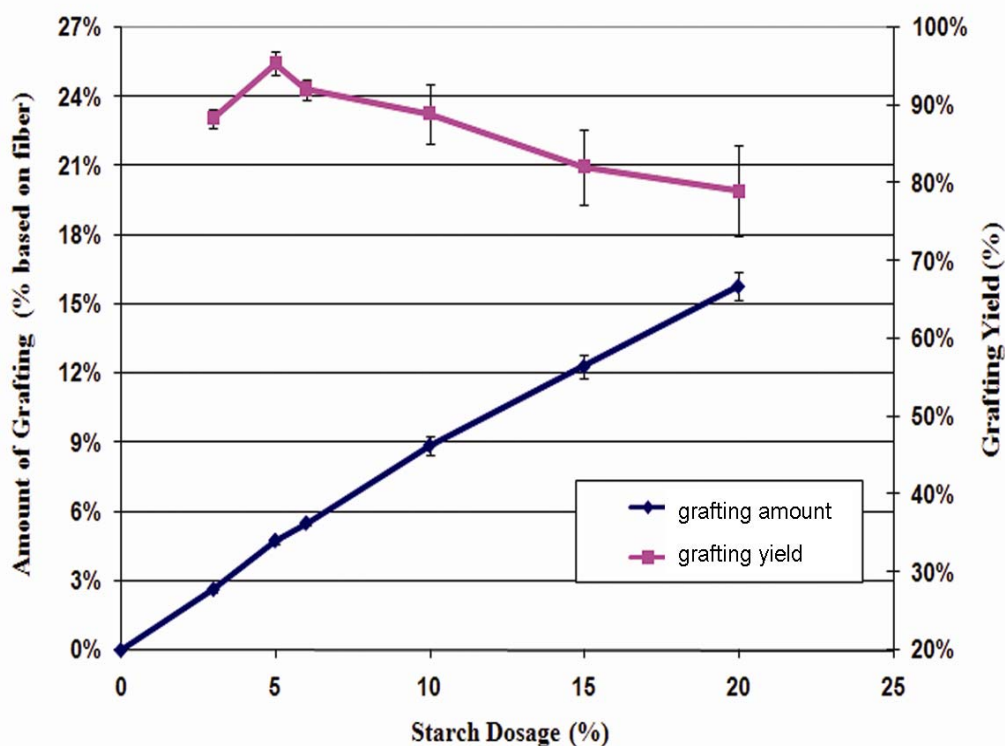


Figure 5.8 Effect of starch dosage on grafting amount and grafting yield (pH: 9; fiber consistency: 3%; temperature 95°C, AZC: starch = 1:2).

In order to achieve a good mixing, appropriate stirring must be applied either during the grafting process or post grafting process. The effect of stirring speed on grafting yield was also studied. During the starch grafting process, moderate stirring speeds at the range of 50-400 rpm were chosen in this study. Figure 5.9 indicates that, applying agitation at 100 rpm during grafting process, an optimal grafting yield was obtained. When a higher stirring speed was applied, the grafting yield was decreased. This is because the hydrogel aggregates formed on the fibers (i.e. grafted starch) is soft and high shear force can easily break the hydrogel resulting in a falloff starch hydrogel from the wood fibers. It was noted that if the stirring speed was too low, AZC and starch would form ungrafted hydrogel particles, resulting in a lower grafting yield.

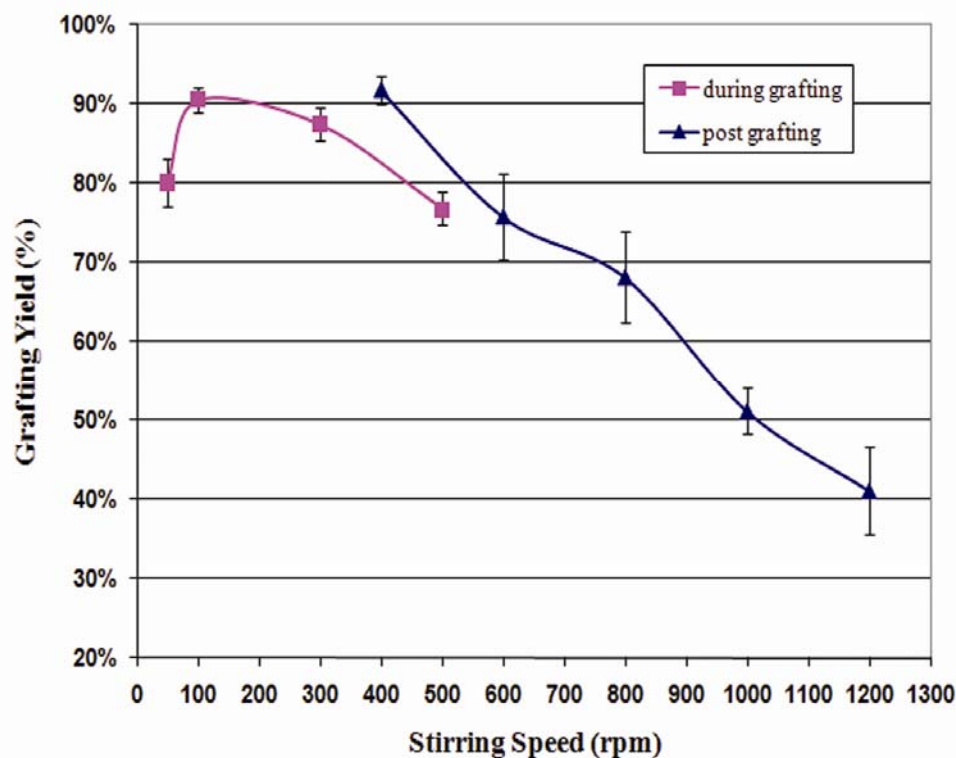


Figure 5.9 Effect of stirring speed on the grafting yield (fiber consistency: 3%; pH 9; temperature: 95°C; starch dosage: 10% based on fiber; AZC: starch = 1:2).

From the microscope pictures, we can see that the surface of modified fibers was covered by starch hydrogel aggregates. The bonding stability of starch hydrogel on wet fibers is an important property which should be considered when setting up the condition of post-processing, such as pumping and stirring in a real manufacture. In this part of study, fibers with 9.5% starch grafting on the surface were used to test the starch bonding stability. After exposing to different shear force, the remaining amount of starch on fibers was evaluated. From Figure 5.9 (post grafting), it can be seen that the grafting yield was remarkably decreased with the increase of stirring speeds. Before drying, the grafted

starch is soft hydrogel with weak strength. Therefore, when processing the slurry of modified fibers, high shear force should be avoided.

5.3.3 Water retention value (WRV) of modified fibers

In many applications, such as drug delivery and diaper, the water retention capability is important. The water retention value (WRV) of fibers is an indication of fibers' ability to take up water. The WRV of fiber can be improved by different ways, such as refining and grafting hydrophilic polymers. The improvement of WRV of fibers by refining is mainly attributed to the increased surface area of fibers. Starch is a typical hydrophilic polymer that can form hydrogel by crosslinking the starch molecules. The starch gel itself is a swellable hydrophilic polymer network which can hold more water than wood cellulose fibers. In this study, the water retention values (WRV) of starch grafted fibers were measured at 23°C. Figure 5.10 shows that WRV of modified fibers was significantly increased with the increase of grafted starch amount on fiber surface.

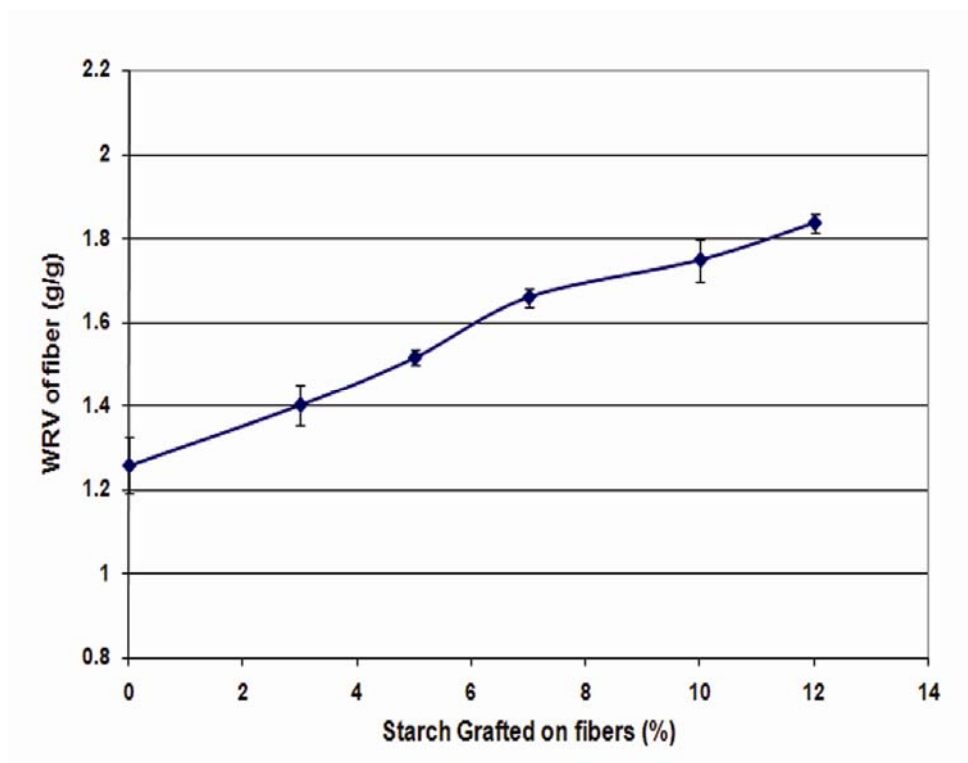


Figure 5.10 The Water retention value (WRV) of fiber vs. starch grafted amount (23°C).

It is reported that WRV is highly correlated to the bonding ability of fibers during paper formation (Biermann 1996). From the results of WRV test, it can be expected, that the bonding ability of starch grafted fibers should be significantly increased, and consequently the paper strength should be improved. In our research, the significant improvements of paper properties, such as tensile strength and stiffness have been demonstrated, and it will be reported in the next chapter.

5.4 Conclusions

In this chapter, a simple and practical technique of fiber modification via starch grafting was developed by crosslinking starch with wood fibers using AZC as the crosslinker. It can be concluded that

- A reasonable amount of starch could be grafted onto fiber surfaces to form “starch fibrils” by hydrogen bond formation among AZC, starch and cellulose molecules.
- The effects of grafting conditions, including pH, temperature, fiber consistency, AZC and starch dosage, stirring speed, on the grafting yield were systematically investigated. Optimal reaction conditions were obtained. (pH: 9; temperature: > 80°C; fiber consistency: 3%; starch dosage: 5%; AZC dosage: 2.5%)
- The soft starch hydrogel grafted on the fiber surface is sensitive to shear force. High shear forces should be avoided during post processing.
- Starch grafting treatment on fibers could significantly improve the water retention value of fibers.

CHAPTER 6

APPLICATION OF STARCH GRAFTED FIBER IN PAPERMAKING

Abstract

In order to improve paper strengths, many techniques, such as fiber refining and the addition of dry strength additives, have been developed and applied in the papermaking process. However, there are some disadvantages of these conventional methods, including a high energy/chemical cost and low drainage rates during the web formation. In Chapter 5, the grafting of raw starch onto wood fibers was studied. It is believed that the grafted starch can function similarly to wood fibrils generated by refining, and therefore the fiber bonding capability can be improved. In this chapter, the effects of starch grafting on water drainage, water removal in the press and drying section, and the paper strength properties were investigated. The repulping of the dry pulp board made of starch grafted fibers was also studied. We found that, compared with the paper sheets made of fibers with an industry refining level (420 ml CSF), the paper sheets made of fibers with a much lower refining degree but with grafted starch show higher paper strengths, including tensile strength, stiffness and z direction tensile (ZDT); meanwhile, a higher drainage rate and water removal rate in the press and drying process were also achieved.

6.1 Introduction

For most of printing/writing and packaging paper grades, paper physical properties, such as tensile strength, stiffness, tear strength, fold endurance, are very important for both converting and the final uses (Okomori, Enomae et al. 1999). On the other hand, for modern paper machines with high machine speeds, a high drainage rate and water removal rate during pressing and drying must be achieved to keep good machine runnability. It is believed that higher drainage rates and water removal rates could be obtained when using less refined fibers or adding fillers (Allan, Carroll et al. 1997; Dong, Song et al. 2008; Zhao, Kim et al. 2008). Unfortunately, the paper strength is relatively low in such situation, particularly for highly filled grades. Therefore, the paper strength must be improved, either by adding dry strength agents or via modification of fiber/filler. Essentially, most of approaches developed for improving paper strength target on the increase of bond strength per unit area or relative bonded area.

In order to obtain high paper strength, some common dry strength additives, such as modified starch, gum and polyacrylamide (PAM), are normally added at the wet end of papermaking (Biermann 1996). Cationic starch is the most commonly used dry strength agent for most of paper grades. It is believed that the increase of paper strength is attributed to the increased number of bonding sites between fibers provided by starches. Although it is a long time practice to use cationic starch, there are still some limitations for its application, including high chemical cost, limited adsorption amount on fibers, poor retention in recycled furnish or at high anionic trash conditions, poor sheet

formation and slow drainage at high starch dosage levels. Furthermore, the strength improvement is limited, usually less than 10%.

As a physical treatment, fiber refining is a common technology adopted in papermaking process for improving paper dry strength (Biermann 1996). Although refining can significantly improve paper strength properties, such as tensile, ZDT, folding, etc., some properties, such as fiber stiffness, would be detrimentally affected. Furthermore, the high energy cost of refining is another concern.

In the aspect of chemical treatment, many fiber modification approaches have been proposed, including fiber wall crosslinking, layer-by-layer (LbL) nanocoating, polymer grafting onto fibers, and fiber charge enhancement (Stamm 1959; Zara, Erdelyi et al. 1995; Biermann 1996; Kling 2001; Pulat & Isakoca 2006; Zheng, McDonald et al. 2006; Lvov, Grozdits et al. 2007; Rahman & Khan 2007; Zhang & Ragauskas 2007; Wang & Deng 2008). However, for all above methods, either high cost chemicals are used, or complicated processes are involved.

A simple, practical and low cost approach for fiber modification should be developed. Using the low cost raw starch directly might be a simple and economically effective way. In chapter 5, the grafting of raw starch on wood fibers was studied, and it was found that large amount of starch could be successfully grafted on fiber surface. It is believed that the grafted starch can function similarly as wood fibrils generated by refining, and therefore the fiber bonding capability can be improved. In this chapter, the starch grafted fibers were used to prepare handsheets and dry pulp board. The physical properties of

paper sheets were measured. The effects of starch grafting on water drainage and the water removal rate in press and drying section were also evaluated.

6.2 Experiments

6.2.1 Materials

The market pulp sheets (bleached softwood kraft pulp) with an initial Canadian Standard Freeness of 750 ml were used in this study. The pulp was refined to different freeness levels with a Valley beater. The raw corn starch (B200) and raw potato starch X100 were provided by Grain Process (Muscatine, Iowa USA). The starch was cooked for 40 minutes using a rotary evaporator at 95°C. Ammonium zirconium carbonate (AZC) was purchased from Aldrich, USA, and used as a crosslinker.

6.2.2 Methods

Fiber modification procedure

Fiber modification via starch grafting was conducted according to the procedure described in chapter 5. The basic process of grafting was to add crosslinker into fiber slurry first and then add precooked starch.

Drainage test

The drainage test was performed by using a Dynamic Drainage Analyzer (DDA). The description of the equipment and the related mechanism were discussed in a previous publication (Dong, Song et al. 2008). Simply, with a shear force in stock and vacuum applied, the DDA can simulate the water drainage on paper machines.

Handsheet Preparation

Handsheets were prepared by using a British Handsheet Mold according to the standard TAPPI method T205 “Forming Handsheets for Physical Tests of Pulp”. No retention aid or dry strength additive was used for all handsheet samples. After wet-press, the handsheets were dried at 105°C with an Emerson speed dryer (Portland, Maine). The handsheets were conditioned at 25 °C and 50.0% relative humidity overnight for the further physical properties tests.

Water removal tests during pressing and drying

The study of wet pressing was conducted by using a MTS Press testing apparatus. The prepared wet handsheets were pressed under a certain pressure (1040 psi) for 3 cycles. The contact time for each press cycle is about 0.03 s. The mass of sheet samples before and after press was measured immediately. The pressed sheet was dried with a Mettler

Toledo[®] LJ16 moisture analyzer, and the weight of the sheet was recorded every 20 seconds. The rate of water removal during drying was calculated accordingly.

Preparation and evaluation of dry pulp board with starch grafted fiber

Pulp boards at a target basis weight of 500g/m² were made of starch grafted fiber by using a British Handsheet Mold. No retention aid or dry strength additive was used for pulp samples. After wet-press, the samples were dried at 105 °C with an Emerson speed dryer (Portland, Maine). The prepared dry pulp boards were then repulped via disintegration and refining, and the handsheets at a target basis weight of 100g/m² were prepared according to the standard TAPPI method.

Paper property test

Tensile strength, Gurley bending stiffness, Z direction tensile (ZDT), folding endurance of handsheets were tested according to TAPPI Test Method T494 “Tensile properties of paper and paperboard”, T543 “Bending resistance of paper (Gurley-type tester)”, T541 “Internal bond strength of paperboard (z-direction tensile)”, T511 “Folding endurance of paper (MIT tester)” respectively. Bulk and opacity of handsheets were measured according to TAPPI Test Method T220 “Physical testing of pulp handsheets” and T425 “Opacity of paper” respectively.

6.3 Results and Discussion

Fiber refining is a current process of fiber modification for improving fiber bonding capability. Under mechanical treatment, the fibers become more flexible and large amount of tiny fibrils can be generated on fiber surface. Consequently, more contact areas between fibers can be created and higher paper strength can be achieved. The refining level can be determined by a standard measurement of freeness, *i.e.* the Canadian Standard Freeness (CSF) test which determines the rate of drainage of a dilute pulp suspension. The unit of freeness is ml CSF. Because the created surface area on fiber surface or inside fibers by refining can hold more water during drainage, the rate of drainage is normally decreased with refining. The higher the refining level, the slower the drainage rate, and the lower the fiber freeness. The initial freeness of market softwood fiber is around 650-750 ml CSF. In paper mills, softwood fibers are normally refined to a relatively high degree around 400-480 ml CSF. In this study, the freeness of 420 ml was considered as the industry refining level, and the fibers with 420ml CSF were chosen as the control samples. The drainage rate, water removal rate in press and drying, and the paper strength properties of fibers at a much lower refining degree but with grafted starch were compared to those of the control fibers with a industry refining level of 420ml CSF.

6.3.1 Effect of the starch grafting treatment on water removal during papermaking

6.3.1.1 Effect of starch grafting on the drainage time

In order to determine the effect of starch grafting on water drainage during web formation, the drainage time of ungrafted fibers and starch grafted fibers at different refining levels was measured by using a dynamic drainage analyzer (DDA). From Figure 6.1, it can be seen that for ungrafted fibers, the drainage time significantly increased with the increase of the refining levels, which is one disadvantage of fiber refining. The results also indicate that at a given refining level, the drainage time was increased after starch grafting treatment (10% starch based on fiber). This is because the grafted starch hydrogel intends to hold relatively large amount of water during drainage. One of the objectives of this study was to compare the drainage performance of starch grafted fibers with that of conventional industry refined fibers. It can be seen that for both unrefined or slightly refined fibers (i.e. at the freeness levels of 750ml and 700ml), the drainage time of grafted fibers was still much shorter than that of conventional industry refined fibers (with 420ml CSF). That means the starch grafted fibers have a better water drainage performance than the conventional industry refined fibers. Therefore, from the aspect of drainage, the starch grafting treatment is more attractive than fiber refining.

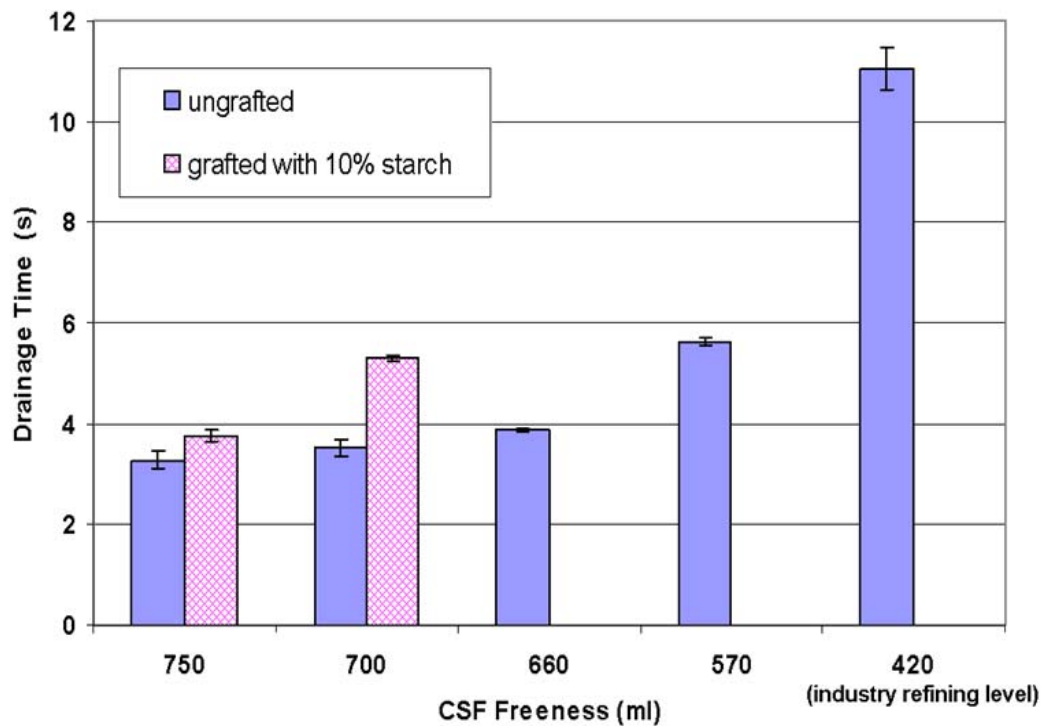


Figure 6.1 Effect of the starch grafting treatment on the drainage time.

6.3.1.2 Effect of starch grafting on water removal in the wet pressing section

In the wet press section of papermaking, water, mainly the free water in sheet, is removed by mechanical means. On paper machines, the typical water content of web leaving press section is about 45-55%. The pressing behavior of paper sheets is highly dependent on fiber properties, which is determined by fiber species, fiber refining levels, and the surface treatments. In this study, the effect of refining and starch grafting on the water removal in wet pressing was determined by measuring the water content of sheets after pressing. In order to simulate multi-nip press on paper machines, press with multi cycles was conducted. The ingoing water content of the sheets was about 75%. Figure 6.2 shows that the water content of the sheets made of fibers at the industry reining level (420 ml CSF) was higher than that of sheet made of slightly refined fibers (700 ml CSF), which

indicates that refining can cause a worse water removal during wet press (Biermann 1996). This is one drawback of refining because the higher water content in wet web would consume more energy during the following drying step. As mentioned previously, the fibers at the industry refining level (420ml CSF) are commonly used in industry. In this study, we consider the water remove performance of such fibers as the control experiments. Any improvement on reducing of water content during wet press would lead to energy saving. It can be seen in Figure 6.2 that for fibers with starch grafting treatment (up to 10% starch based on fiber), the water content of wet web after press was reduced to 47-50%, which is 2-5% points lower than that of fibers at an industry refining level. This improvement in water removal during the wet pressing would directly result in considerable cost savings. It has been suggested that, for 1% solids content increase in the press section, 4% energy can be saved in the drying section (Bermond 1997).

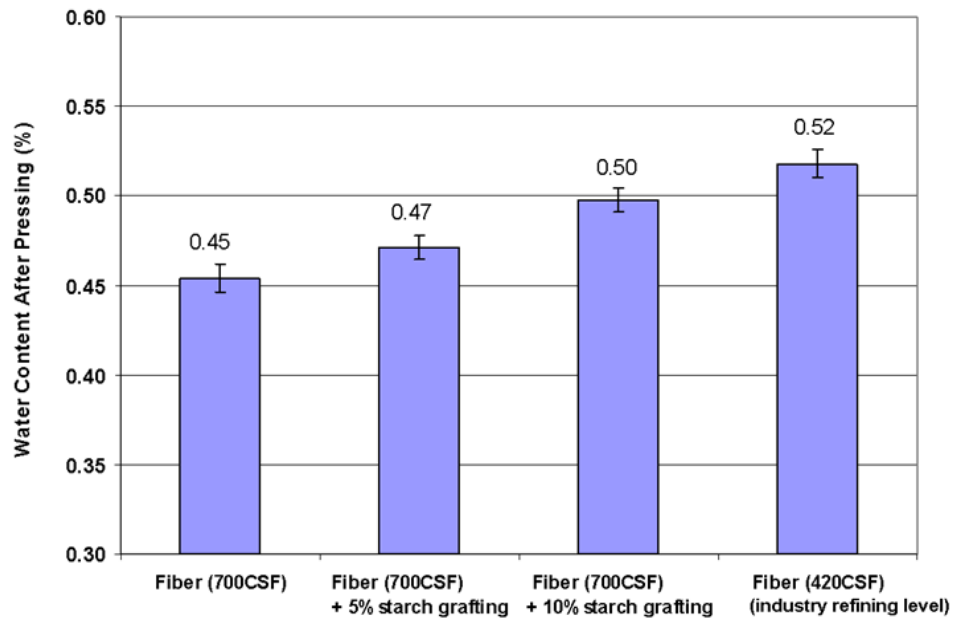


Figure 6.2 Water contents of the paper sheets after 3 cycles of pressing under 1040 psi.

6.3.1.3 Effect of starch grafting on water removal during drying

After water removal in the press section, the remained free water within fibers and the bound water on fiber surface via hydrogen bonding needs to be removed via the thermal drying. In order to evaluate the pure effect of drying section, the initial solids contents of all sheets were adjusted to the same level (53%). The percentage of water removal over time for different samples is illustrated in Figure 6.3. During the drying process, the difference of water removal between different samples was demonstrated. As the control sample in this study, the sheets made of fibers at the industry refining level (420ml CSF) show the lowest water removal rate. For example, after 80s of drying, about 82% of water was removed from the sheets made of starch grafted fibers, while only 77% of total water was removed for the sheets made of the fibers at the industry refining level (420 ml CSF). This suggests that during drying the water removal rate of fibers with grafted starch was faster than that of fibers at the industry refining level.

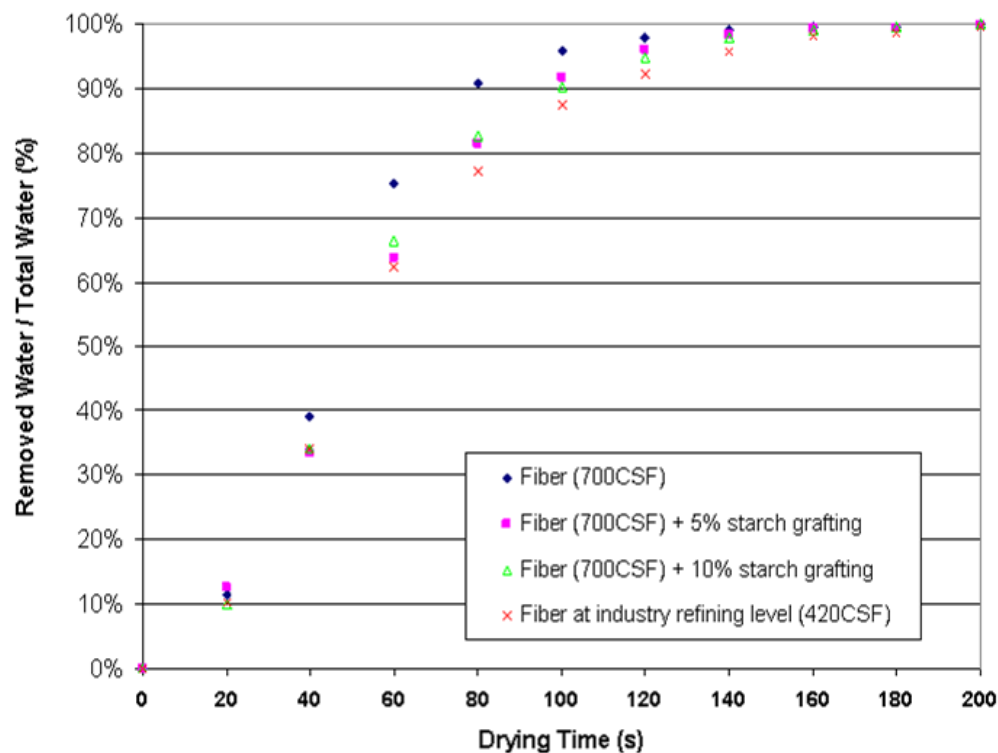


Figure 6.3 Effects of starch grafting on water removal during drying.

The above results illustrate the difference of water removal behavior for different fibers during sheet formation (drainage), wet pressing and drying. The objective was to compare the water removal performance of starch grafted fibers with that of fibers at an industry refining level (420ml CSF). All the test results suggest that, for unrefined or slightly refined fibers, starch grafting treatment can maintain an advantage on water removal over the conventional refining treatment.

6.3.2 Effect of the starch grafting treatment on paper strength properties

6.3.2.1 Preliminary results: high amount of starch grafting on fibers

In the preliminary study, 10% starch (based on fibers) was grafted on fibers and these modified fibers were used to make handsheets. The morphology of starch grafted fibers was already demonstrated in Figure 5.3 and discussed in chapter 5. In this chapter, we will pay more attention to the effect of starch grafting on paper strength properties. With such a large amount of starch (10%) grafted on fibers, the strength properties of handsheets are expected to improve significantly. From Figure 6.4, we can see that, the starch grafting treatment could increase the tensile strength of handsheets at all refining levels. For unrefined fibers (i.e. at the initial freeness of 750ml CSF), the increase of tensile index caused by starch grafting was remarkable, more than 200%. As we mentioned, 420 ml CSF refers to an industry refining level. In this study, the paper made of fibers at an industry refining level of 420ml CSF was chosen as the control sample. Figure 6.4 shows that for slightly refined fibers (at 700ml CSF) with grafted starch, the tensile index of handsheets was higher than that of the control handsheets made of fibers at industry refining level (i.e. 420 ml CSF). This suggests that the starch grafting treatment can provide a higher paper tensile strength than the conventional refining process. As a result, a big saving of refining energy cost can be achieved. For the fibers with higher refining levels, the tensile index could be further increased by starch grafting treatment. But the increase was not significant, and eventually reached to a level-off value.

We believe that the mechanism of the tensile strength increase is related to the increase of bonding numbers. During pressing and heating of handsheets, the small starch hydrogel particles chemically grafted on fiber surface can deform into very thin films and distribute among fibers/fibrils (Figure 6.5). Consequently, more hydrogen bonds can be formed between fibers and starches because more contact areas was generated. Therefore, the tensile strength of paper is increased.

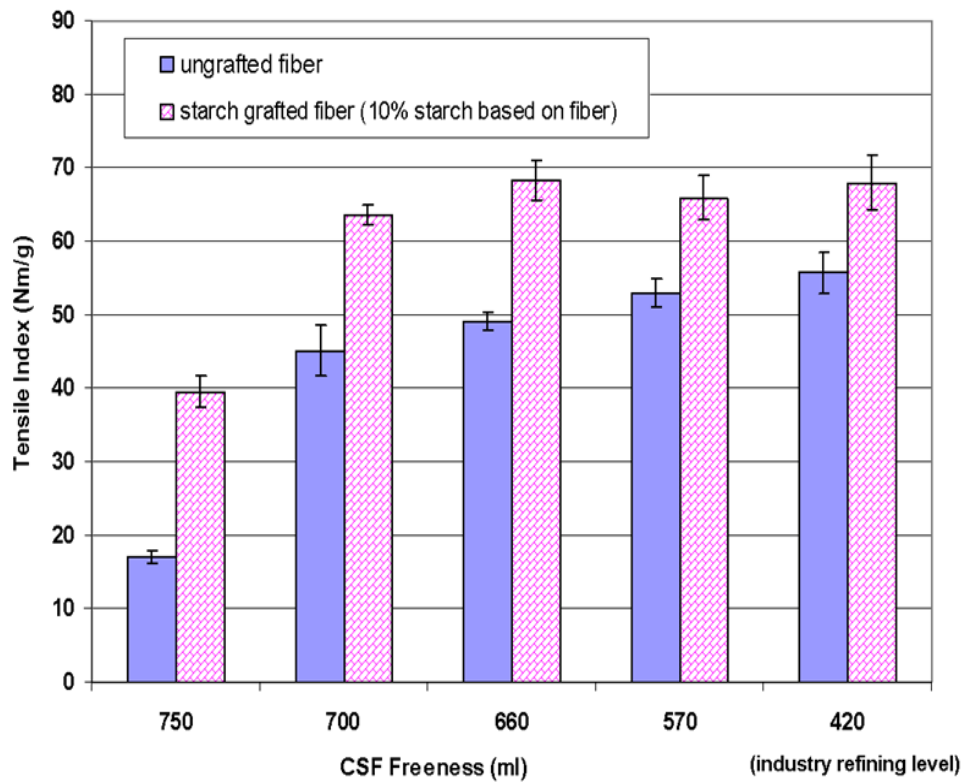


Figure 6.4 Effect of starch grafting treatment on the tensile strength of handsheets.

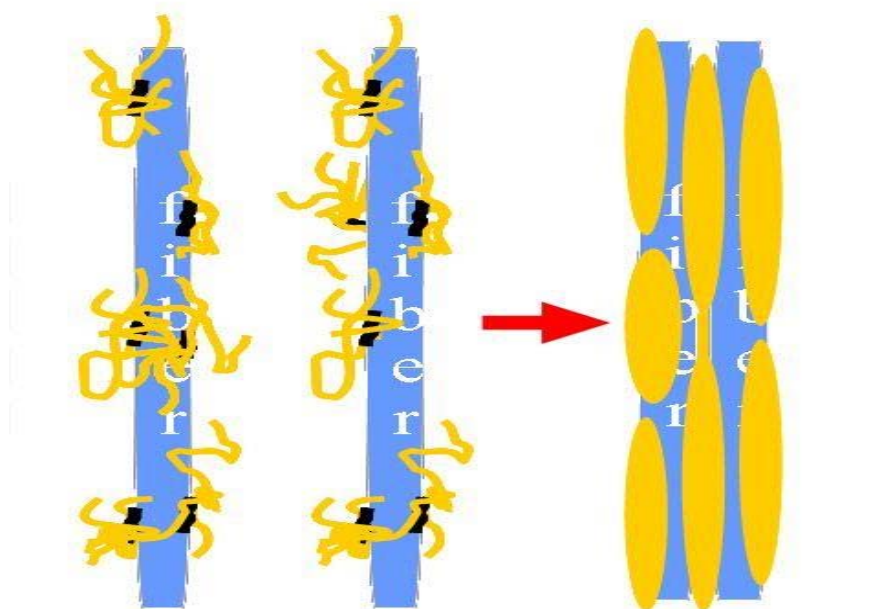


Figure 6.5 A schematic description of fibers grafted with starches.

The stiffness index of handsheets was also determined, and the results are summarized in Figure 6.6. The results show that the stiffness indices were increased by starch grafting at all refining levels. For unrefined or slightly refined fibers (700-750mlCSF) with the starch grafting treatment, the stiffness index of handsheets was much higher than that of the handsheets made of fibers at the industry refining level (420 ml CSF).

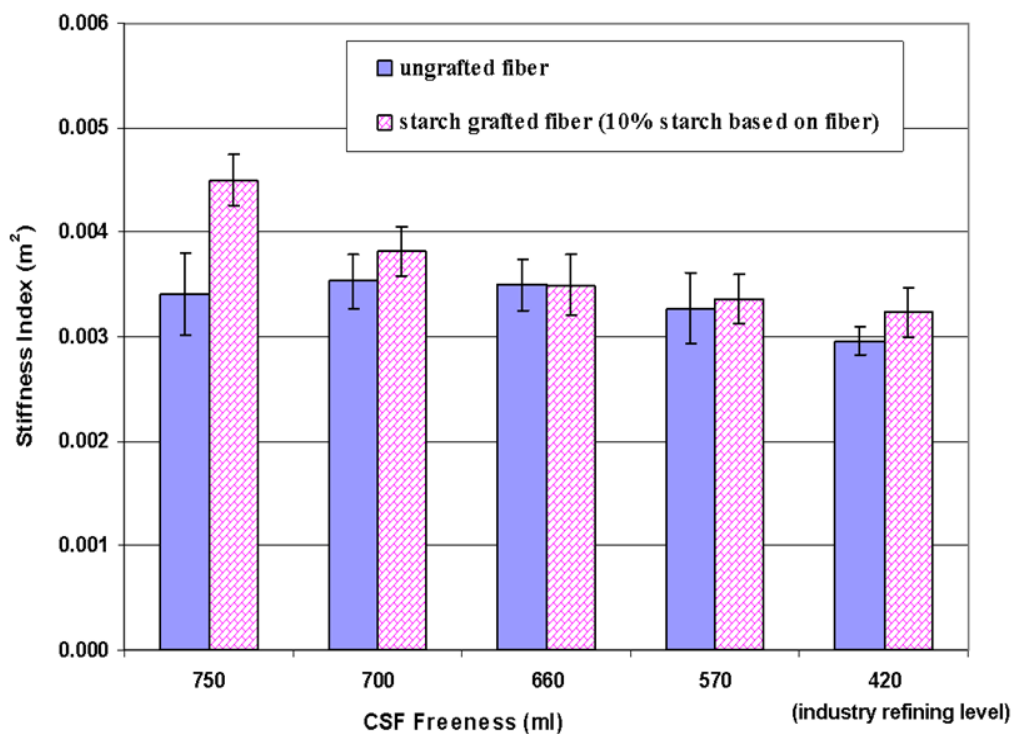


Figure 6.6 Effect of starch grafting treatment on stiffness index of handsheets.

For comparison of the effects of refining and starch grafting treatment, the paper strength properties, including tensile index, stiffness index and z direction tensile (ZDT) are summarized in Figure 6.7. It can be seen that with starch grafting treatment the tensile strength, stiffness and ZDT of handsheets are much higher than those of handsheet made of fibers at an industry refining level of 420 ml CSF. Therefore, from the aspect of improving paper strength properties, starch grafting treatment is more attractive, compared to fiber refining.

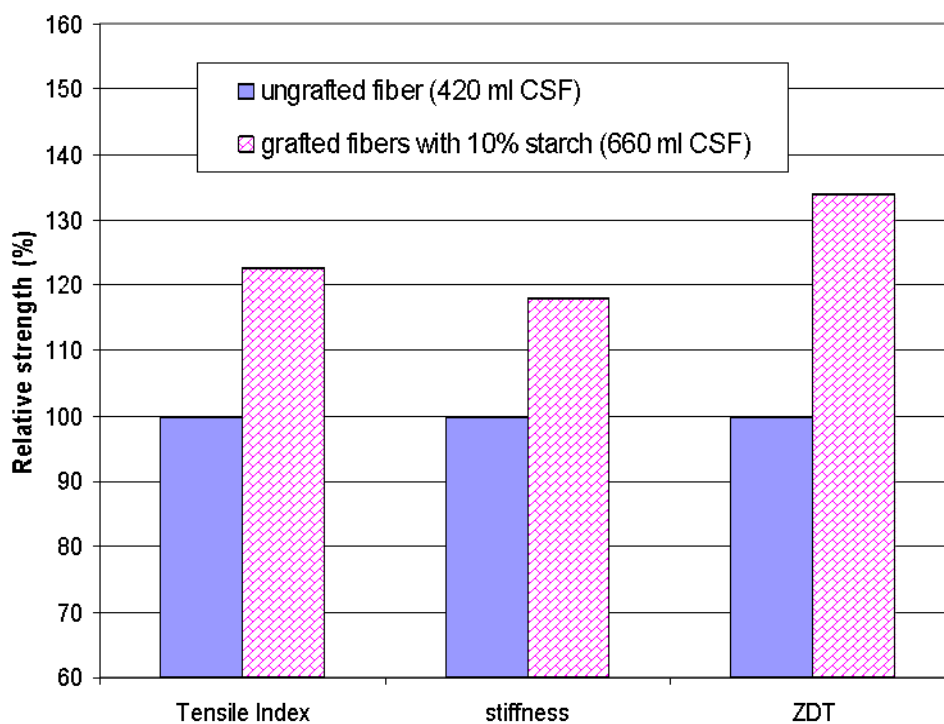


Figure 6.7 Comparison of paper strength properties for different treated fibers.

The other physical and optical properties of handsheets, such as bulk and opacity were also measured. From Figure 6.8, we can see that with the starch grafting treatment, the paper bulk decreased slightly, but was still much higher than that of paper made of fibers at an industry refining level of 450 ml CSF. Similarly, the opacity of handsheets made of starch grafted fibers was higher than that of the handsheet made of fibers at an industry refining level of 450 ml CSF, which means starch grafting is more attractive than the conventional fiber refining process. In addition, it was observed that the formation of handsheet made with starch grafted fibers was comparable to that of handsheets made of fibers at the industry refining level.

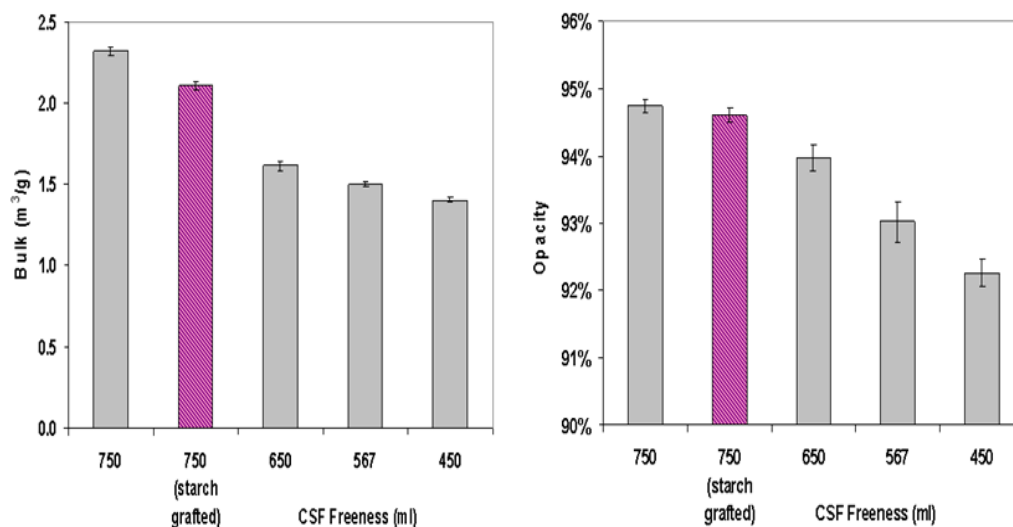


Figure 6.8 Bulk (left) and opacity (right) of handsheets at different refining levels.

6.3.2.2 Optimization of starch dosages and AZC dosages for starch grafting

Effect of starch dosage on physical properties of handsheets

In paper industry, the typical dosage of cationic starch is around 1% (based on fiber). When higher dosage of cationic starch is used, some practical problem would occur, such as low retention rate of starch, and bad formation of paper sheet. As demonstrated in previous sections, a large amount of starch (up to 10% in this study) can be grafted on fiber surface and the formation of paper sheet is also good, which are two benefits of starch grafting treatment. However, it is fundamentally interesting to know what relationship between starch amount on fibers and the paper strength properties. By understanding this relationship, the optimized amount of starch for practical production might be proposed. In this part of study, slightly refined fibers at 615 ml CSF was used, and 3% AZC based on fibers was added. The physical properties of paper treated at

different starch grafting dosages were shown in Figures 6.9 to 6.11. The results indicate that the paper strength properties (tensile index, ZDT and stiffness) increased with the increase of starch dosage first, and then reached a level-off value at 5-10% starch addition. That means when starch dosage is above 5%, further increase of starch would not improve the paper strength considerably. In addition, when 3% starch was grafted on slightly refined fibers, the resultant paper strength was equivalent to (tensile strength and ZDT) or even higher than that of handsheet made of fibers at industry refining level (420 ml CSF). The above results indicate that 3% starch addition might be an optimal option for practical production.

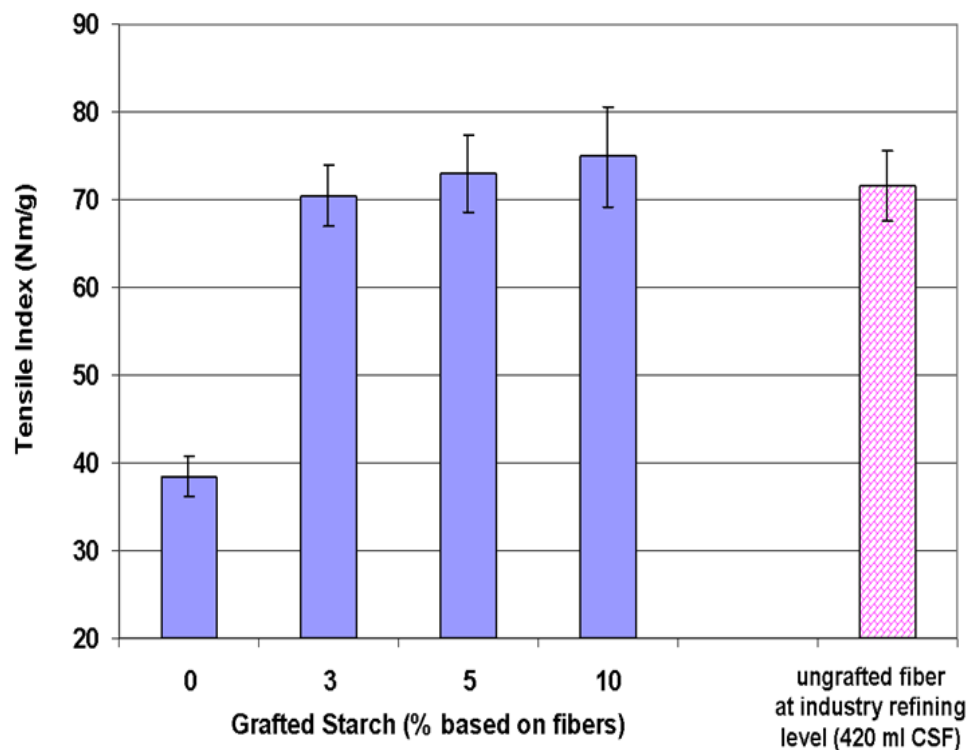


Figure 6.9 Tensile index vs. different starch dosages for the grafting treatment (615 ml CSF pulp, 3% AZC).

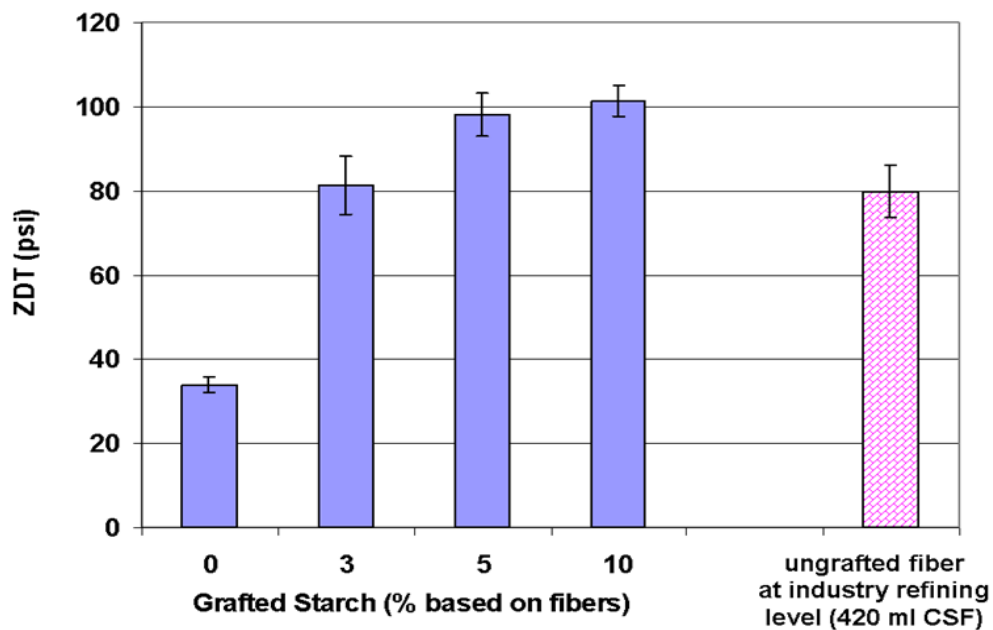


Figure 6.10 ZDT vs. different starch dosages for grafting treatment (615 ml CSF pulp, 3% AZC).

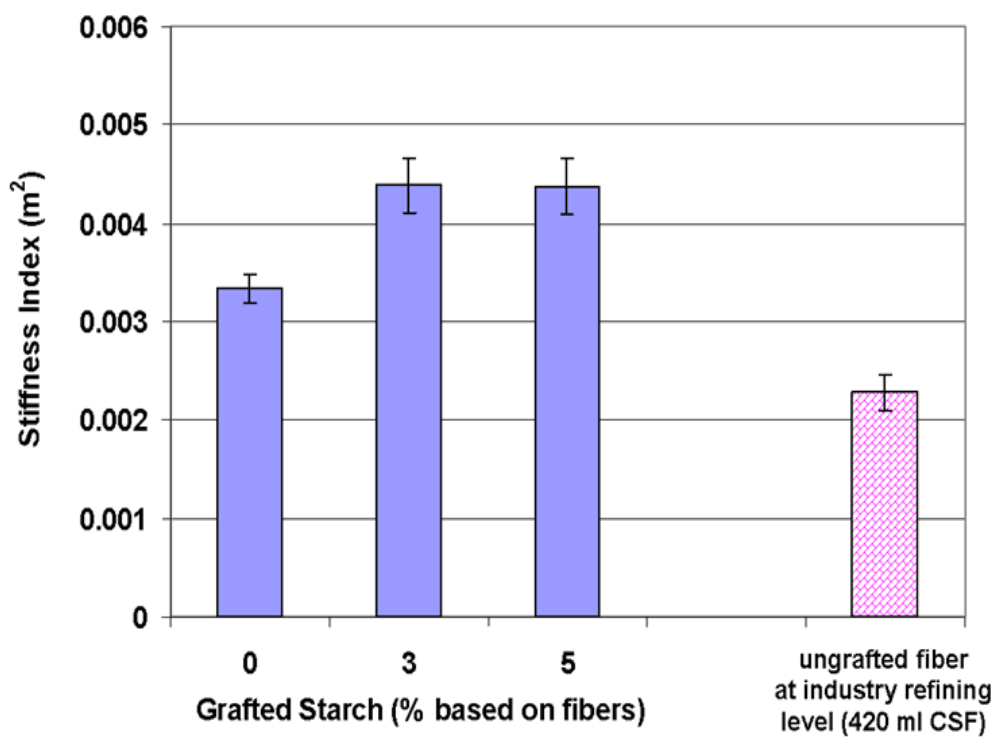


Figure 6.11 Stiffness index vs. different starch dosages for grafting treatment (615 ml CSF pulp, 3% AZC).

Effect of AZC dosages on strength properties of handsheets

For the grafting process, AZC acts as a crosslinker or a coupling agent between cellulose fiber and starch. Therefore, the dosage level of AZC is very important for the starch grafting efficiency on fibers which would highly impact the strength properties of paper made of the grafted fibers. In this part of study, the effect of AZC dosages on paper strength properties was investigated by varying the AZC dosage while fixing the starch dosage at 3% (based on fiber). The results of the paper strength properties are illustrated in Figures 6.12 to 6.14. It can be seen that with the increase of AZC dosages, the paper strength (tensile index, ZDT and stiffness) was first increased, and then decreased slightly at a high AZC dosage. This means, for a fixed starch dosage, when AZC amount is above a certain threshold, the paper strength properties could not be further improved. A similar trend was found in a previous research in the effect of the crosslinker dosage on the grafting efficiency (Song, Zhao et al. 2009). As AZC can react with both cellulose fiber and starch, starch can be crosslinked and grafted on fiber surface. The grafted starch would be remained in the paper sheet, and significantly improve the fiber-fiber bonding capability, resulting in improved paper strength properties. At an appropriate AZC dosage, AZC can distribute evenly on fiber surface, and only limited AZC hydrogel with a small aggregate size can be formed. However, if the amount of AZC in the fiber slurry was too high, the self-crosslinking of AZC would occur extensively, and AZC hydrogel aggregates with larger size would be formed on fiber surface. When the cooked starch was added, only part of starch can be grafted well on fibers because there might be not enough active sites left on AZC due to its self-crosslinking. In addition, most of the

starch would be grafted on the aggregates of AZC hydrogels so that a good distribution of starch on fiber surface can not be achieved. Consequently, the paper strength would be decreased due to the reduced grafting amount of starch and uneven distribution of grafted starch on fiber surface. Considering both the paper properties and the high cost of the crosslinker, 1-2% AZC based on fibers might be a reasonable choice for the grafting treatment when 3% starch is added.

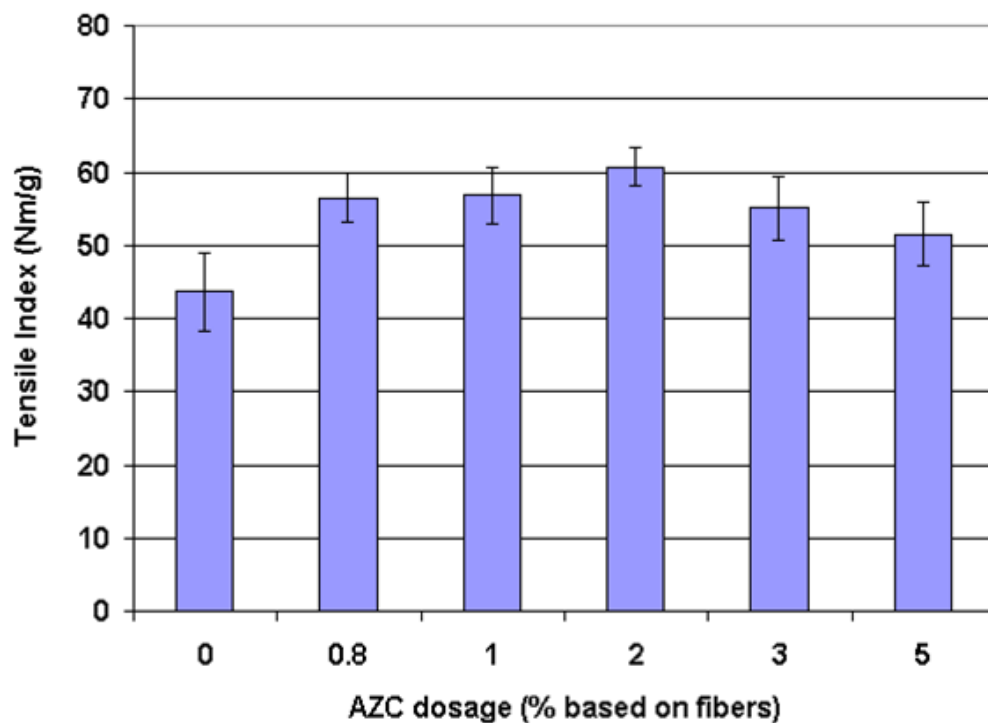


Figure 6.12 Tensile index vs. different AZC dosages for the grafting treatment (615 ml CSF pulp, 3% starch).

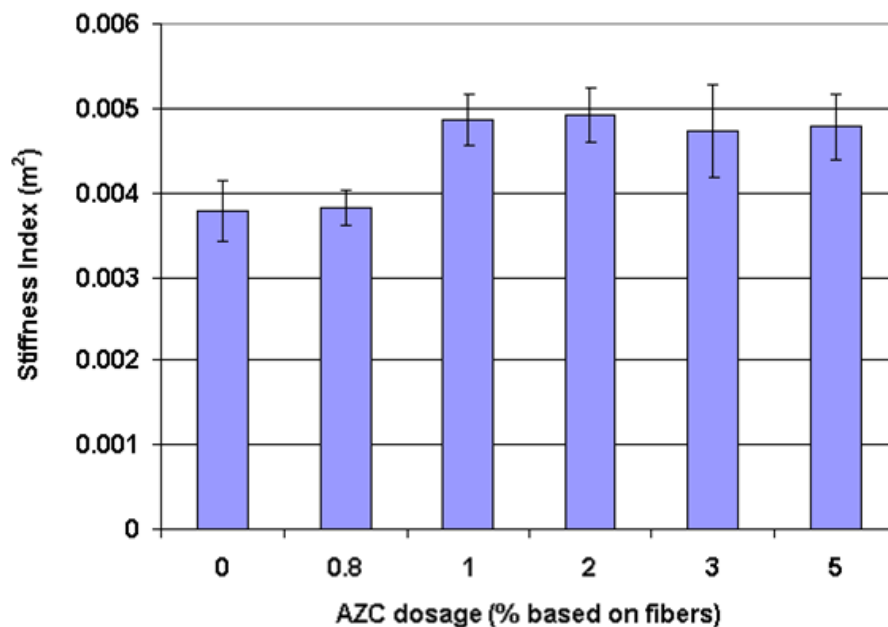


Figure 6.13 Stiffness index vs. different AZC dosages for the starch grafting treatment (615 ml CSF pulp, 3% starch).

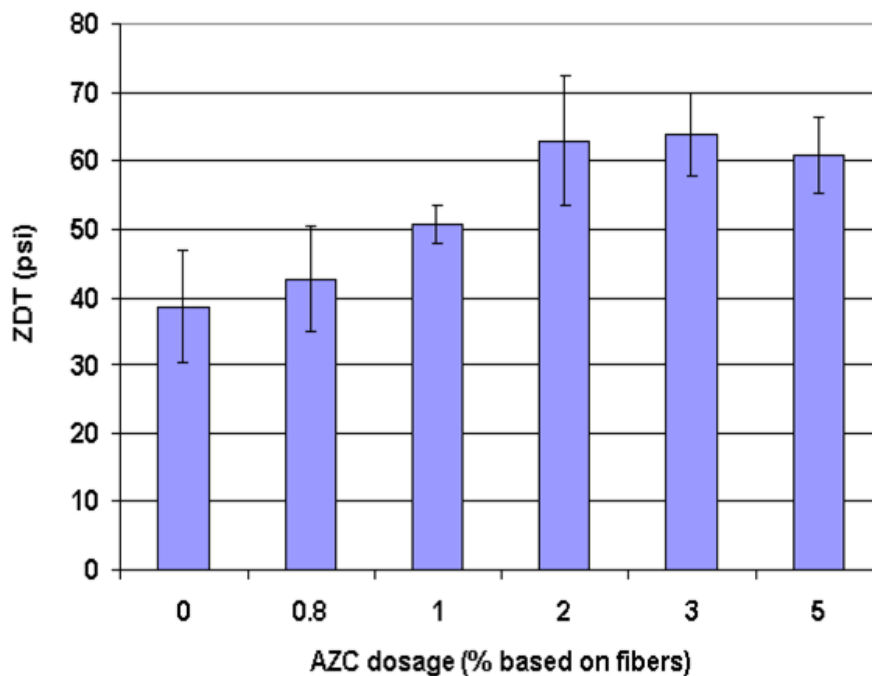


Figure 6.14 ZDT vs. different AZC dosages for the starch grafting treatment (615 ml CSF pulp, 3% starch).

6.3.3 Repulping of dry pulp boards made of the starch grafted fibers

In the previous sections, it is well demonstrated that large amount of starch could be grafted on fiber surface by using AZC as a crosslinker. For slightly refined fibers with starch grafting, faster drainage and water removal in press and drying section, and higher paper strength were achieved, compared to the fibers at industry refining levels. However, whether the paper made of starch grafted fibers can be easily repulped, and whether there is a significant strength loss due to repulping are of great interest not only for fundamental understanding but for practical applications. In this section, the experimental was designed to conduct dry board repulping and paper strength property evaluation.

6.3.3.1 Repulping process of the dry pulp boards made of starch grafted fibers

In this study, 3% starch (based on fiber) was grafted on slightly refined fibers (615 ml CSF), and pulp board with a basis weight of 500 g/m² was prepared by using the grafted fibers. It was observed that the prepared dry pulp board could not be dispersed into individual fibers by using the routine repulping methods, such as the disintegration process. The pretreatment with heat and alkaline (pH to 10-11), and high mechanical shearing forces were tried to repulp the dry pulp board. Although the fibers of dry pulp board were well dispersed, the handsheet prepared with those repulped fibers demonstrated considerable strength loss. This is because that the strong mechanical treatments caused damage for the grafted starch: part of the grafted starch on fibers was

broken into small pieces which are separated from fibers, and drained away during the handsheet formation. A long-time heating or alkaline treatment could also soften the grafted starch, resulting in the breaking up of starch from fibers during repulping.

Slightly refining was finally found to be an effective way to disperse the starch grafted fibers in the dry pulp board with less damage on the grafted starch. After heated at 90°C for 10 minutes, the pulp board was disintegrated at 5000R, and then refined slightly (1000R) with a PFI refiner. The optical microscope images (Figure 6.15) illustrate that after repulping there are still large amount of starch bonded on fiber surface.

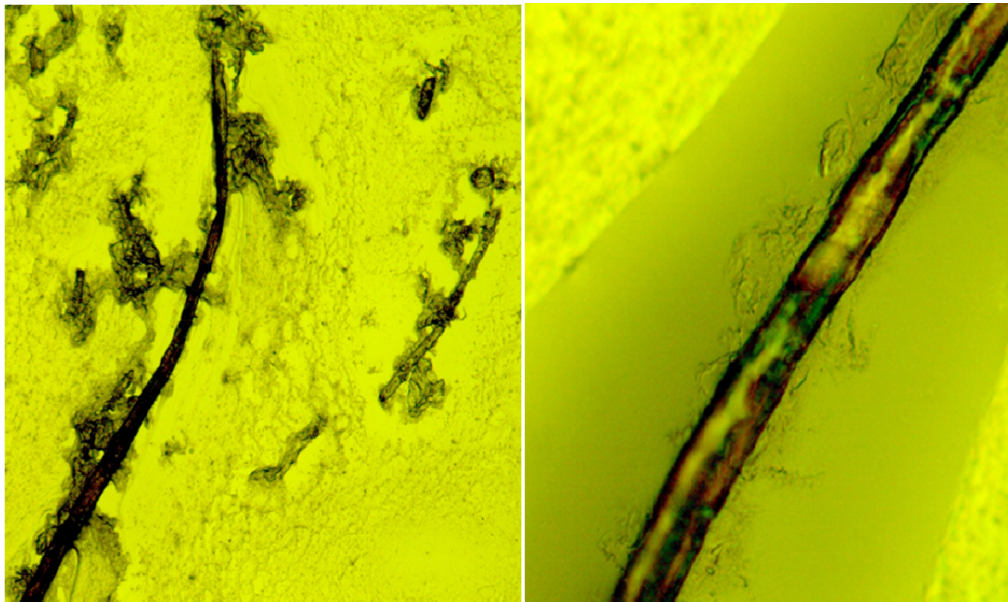


Figure 6.15 Dispersed fibers after repulping with slight refining treatment (initial starch grafting amount: 3% based on fiber).

6.3.3.2 Physical properties of handsheets made of the repulped starch grafted fibers

The dry pulp board with 3% starch grafting treatment was repulped via the process described above, and the handsheets were prepared for strength property tests. Once again, we use the paper strength properties of handsheets made of fibers at industry refining level (420 ml CSF) as the reference values. It can be seen from Figures 6.16 that the handsheets made of the repulped starch grafted fibers show good performances on all tested physical properties. Compared with the reference, i.e. paper made of ungrafted fibers at an industry refining level (420 CSF), the paper made of the repulped starch grafted fibers had slightly higher tensile strength and ZDT. Meanwhile, the bending stiffness was almost 2 times of the reference values. All the above results suggest that the repulped starch grafted fibers have a good potential to be reused for preparing paper sheets.

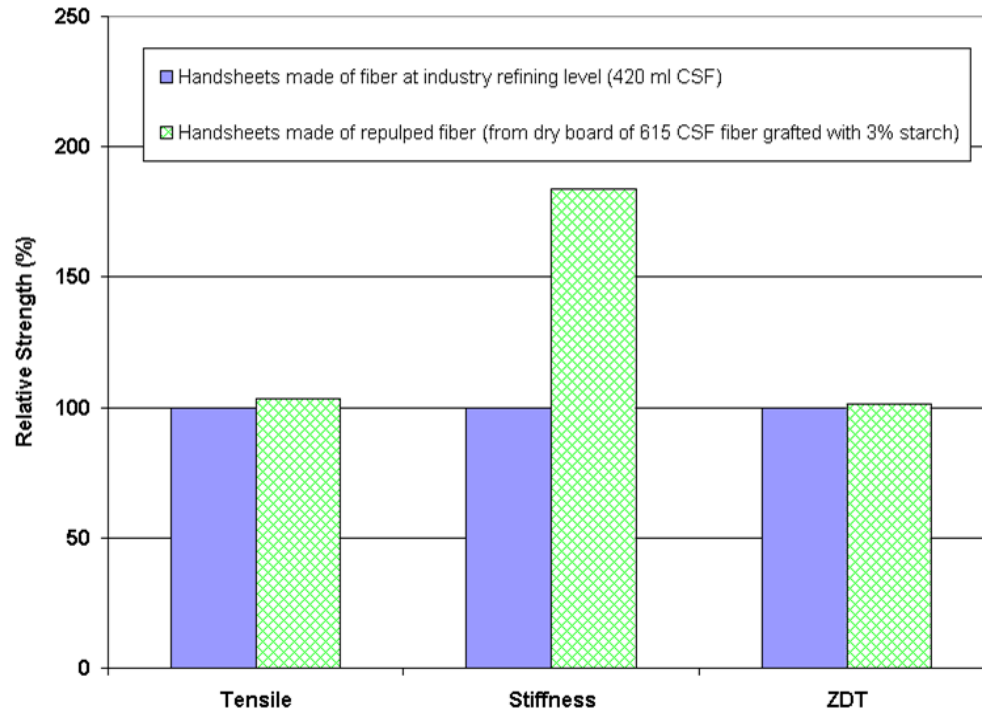


Figure 6.16 The comparison of strength properties of handsheets made of different fibers.

6.4 Conclusions

In this chapter, the effects of starch grafting treatment on water drainage, water removal in the press and drying sections, and paper strength properties were investigated. The repulping of dry pulp board containing starch grafted fibers was also studied.

- Compared with the fibers at an industry refining level (420 ml CSF), the fibers with a much lower refining degree (600-700 ml CSF) but with grafted starches had a much faster water drainage and water removal rates in the wet press and drying process.

- For unrefined and slightly refined fibers, the starch grafting treatment on fibers could significantly improve the strength properties of paper, including tensile, stiffness, and ZDT.
- Compared with the fibers at an industry refining level (420 ml CSF), the fibers with a much lower refining degree (600-700 ml CSF) but with grafted starches had an equivalent or even higher paper strength, including tensile, stiffness and ZDT.
- A high addition level of raw starch (up to 10%) grafted on fibers had little effect on opacity and formation of paper.
- It was found that 3% starch and 1-2% AZC based on fibers are an optimal condition for the starch grafting treatment.
- Slight refining was found to be an effective way to disperse the starch grafted fibers in the dry pulp board with less damage to the grafted starch.
- The handsheets made of the repulped starch grafted fibers gave even higher paper strength properties including tensile, stiffness and ZDT, compared with those made of fibers at an industry refining level (~420 ml CSF).

CHAPTER 7

FILLER MODIFICATION VIA STARCH COATING WITH CROSSLINKERS

Abstract

In chapter 6, it was demonstrated that the fiber-fiber bonding can be improved by grafting starch onto fibers. It was also demonstrated in previous researches the filler-fiber bonding can be also improved if starch can be effectively coated on the filler surface. This concept has been approved by the early studies. However, one of the problems related to starch-coated fillers is the low size stability of particles in water. It is well known that crosslinking may reduce the solubility of starch in water. Therefore, in this thesis work, starch crosslinkers were induced in the process of filler modification to stabilize the starch coating layer in water. It was found that the size stability of starch coated fillers with crosslinkers in water was considerably improved. Surprisingly, it was found that the breaking-up of starch coated fillers have little effect on paper strength, which suggest that the size stability of starch-coated fillers in water is not a major concern for practical applications.

7.1 Introduction

It is a common practice for today's paper industry to add mineral fillers to replace part of fibers. The purposes of filler addition are to reduce cost of raw materials, improve papermaking process, such as drainage and drying, and obtain desired paper properties,

such as high opacity and better printing performance. Unfortunately, the strength of paper with a high filler dosage is decreased because filler particles can interfere fiber-fiber bonding. The low retention of fillers is another problem for papermakers.

In order to increase retention and bonding capability of fillers, filler pretreatment or filler modification has to be done. Many technologies have been developed in the past decades, including filler pre-flocculation technology (Smith 1981; Park & Shin 1987; Mabee & Harvey 2000; Mabee 2001), filler pretreatment with adsorption of strength additives (Novak, Stark et al. 1987; Dunham, Jakubowski et al. 1999; Koper, Vanerek et al. 1999; Vanerek, Alince et al. 2000), filler and wood fines composites (Aho, Silenius et al. 2006), and filler lumen loading (Green, Fox et al. 1982; Middleton & Scallan 1985; Miller & Paliwal 1985). However, most of the above technologies are not suitable for practical applications due to the complicated process or high cost of chemicals.

Recently a novel concept of filler modification via starch coating was proposed by Deng group at Georgia Tech (Yan, Liu et al. 2005; Zhao, Hu et al. 2005; Yoon & Deng 2006a; Yoon & Deng 2006b; Zhao, Kim et al. 2008; Song, Dong et al. 2009). Basically, a very thin layer of starch can be coated on filler particles/aggregates surface either by wet approaches or by dry approaches. Figure 7.1 demonstrates the difference between traditional papermaking process and a new process with starch coated fillers. There are two major advantages to apply these approaches: one is the low cost because of using raw starch; the other one is enhanced filler-filler and fill-fiber bonding. Young and Deng (Yoon & Deng 2006a; Yoon & Deng 2006b) developed a series of wet approaches to

coat filler with starch, including starch-clay composite by $(\text{NH}_4)_2\text{SO}_4$ and starch-clay composite by fatty acid complex. Yan (Yan, Liu et al. 2005) and Zhao et al. (Zhao, Hu et al. 2005) coated starch on clay and PCC particles via a vacuum dry and grinding method, and the paper strength was increased. Zhao and coworkers (Zhao, Kim et al. 2008) also applied a spray dry method to coat clay fillers with cooked raw starch. Both the lab and pilot trial results showed significant improvement of paper strength and energy saving of pressing and drying. However, we found that the spray dried starch-coated fillers are likely to break up into smaller pieces in water. Whether the breaking up of the starch-coated filler would cause negative effect on paper strength is not only fundamentally interesting but also important for practical applications. The objective of this work was to improve size stability of fillers in water by introducing crosslinkers during filler modification, and investigate the effects of particle size of modified fillers on paper strength properties.

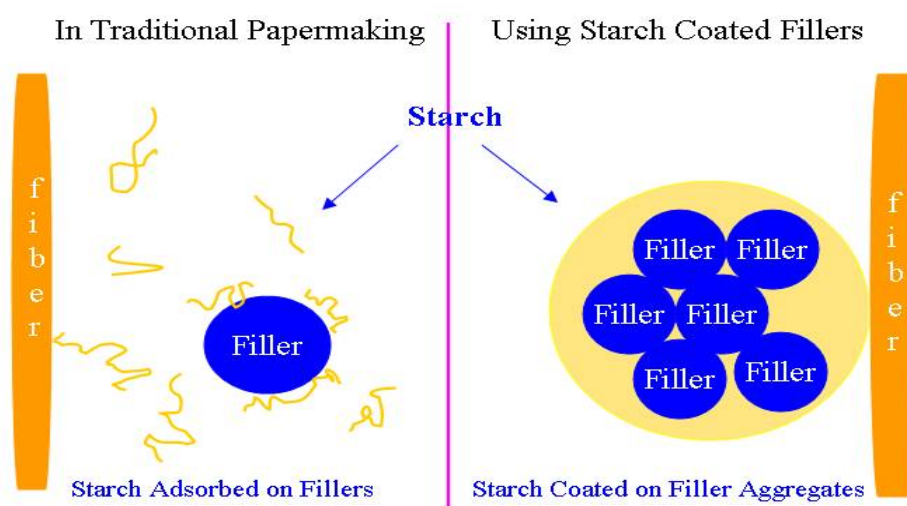


Figure 7.1 Comparison of unmodified fillers and starch coated fillers in papermaking.

7.2 Experiments

7.2.1 Materials

Polyamidoamine-epichlorohydrin (PAE, Kymene 557H) provided from Hercules (Wilmington, DE) and glyoxal based wet strength agent (DPPT 05) provided from Ciba are used as crosslinkers. Raw corn starch B200 was purchased from Graining Processing Corporation. Spray dried clay and conventional clay filler were provided by Imery. The repulped OCC (old corrugated container) pulp was prepared in lab.

7.2.1 Methods

Filler modification via spray drying

- 5% raw corn starch was cooked at 95°C for 40 minutes with a rotary evaporator;
- The mixture of clay, starch and crosslinker were prepared at a solid content of 10% (the ratio of filler : starch: crosslinker = 100: 2.5: 1.25);
- Spray drying was conducted by using the spray dry equipment at IPST.

Microscope observation

The dry powder and rewetted particles (contact with water for 3 hours) of spray dried fillers were observed with a scanning electron microscope (Hitachi S-800 FE-SEM).

Handsheet preparation and tensile strength test

Handsheets were made by using a British Handsheet Mold according to the standard TAPPI method T205 “Forming Handsheets for Physical Tests of Pulp”. No retention aid or dry strength additive was used for all handsheet samples. After wet-press, the handsheets were dried at 105°C with an Emerson speed dryer (Portland, Maine). The handsheets were conditioned at 25°C and 50.0% relative humidity overnight for the further physical properties tests. Tensile strength was tested according to TAPPI Test Method T494 “Tensile properties of paper and paperboard”.

7.3 Results and Discussion

7.3.1 Effect of starch crosslinking on size stability of starch-coated fillers in water

The purpose of filler modification via spray drying is to coat starch on filler particle surface, and enhance the bonding capability of fillers with fiber. In our previous research, only the mixture of precooked starch and clay filler in a certain ratio was prepared. No other chemical additives were added. The particles of spray dried fillers have a sphere shape with average size of 40μm (Figure 7.2 left). However, after the fillers contacted with water for 20 minutes, part of filler particles broke into smaller size pieces (Figure 7.2 right).

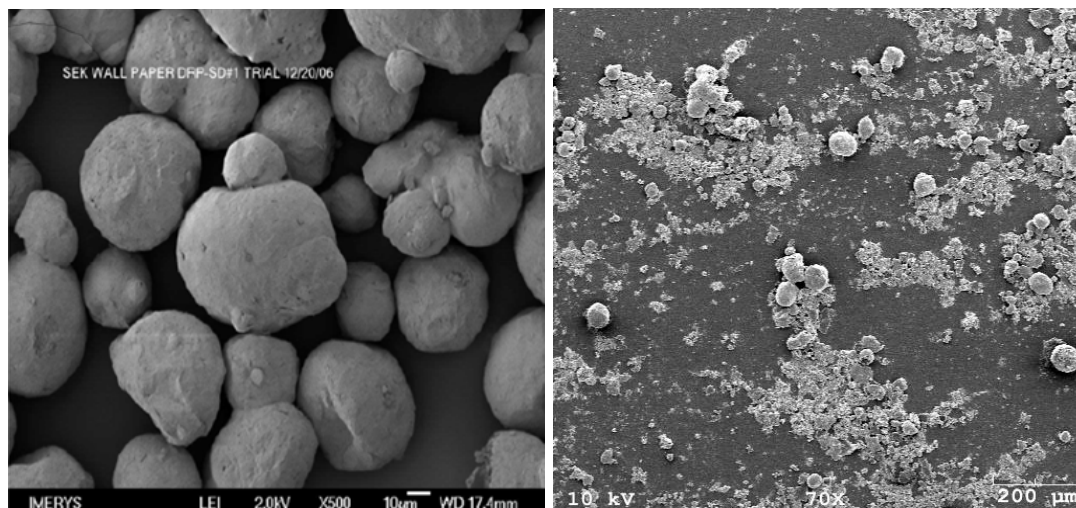


Figure 7.2 SEM pictures of spray dried clay fillers (starch coated without crosslinkers) (left: dry particles; right: re-wetted for 20 minutes)

In order to stabilize the coated starch layer in water, two types of crosslinkers, polyamidoamine-epichlorohydrin (PAE, Kymene 557H) and glyoxal (Ciba DPPT 05), were used. PAE is a typical wet strength agent used in papermaking. When the mixtures of PAE and starch are heated, the self-crosslinking of PAE occurs, and the starch molecules are entrapped in the crosslinked network. As a result, the swelling and dissolving of starch in water can be impeded. The mechanism of starch crosslinking by glyoxal has already been discussed in Chapter 2. Glyoxal has a strong affinity to hydroxyl groups in starch molecules, and acetal bonds are formed between the hydroxyl groups and aldehydes. It is believed that the crosslinked starch has a much lower swelling ability and solubility in water.

Before spray drying, the crosslinker was added into the mixture of precooked starch and fillers. The SEM pictures (Figure 7.3) show that, with both types of crosslinkers, the

spray dried fillers could keep intact shape, i.e. no breaking up after contacting with water for 3 hours. That means the crosslinkers can significantly improve the rewetting stability of spray dried fillers.

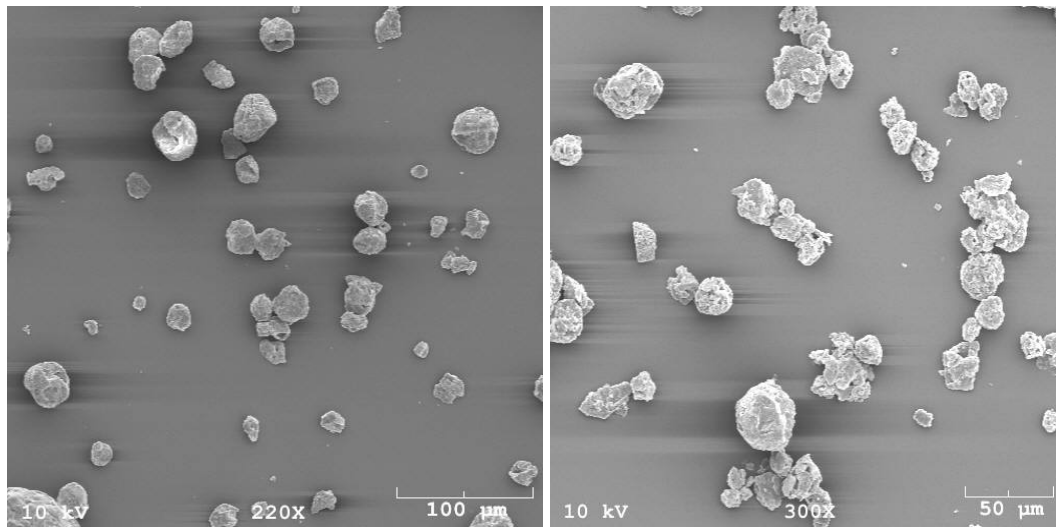


Figure 7.3 SEM pictures of spray dried fillers after 3 hour contact with water (left: with Hercules Kymene 557H ; right: with Ciba DPPT 05).

7.3.2 Effect of starch crosslinking on the tensile strength of paper

Previous reports (Zhao, Kim et al. 2008) showed that the spray dried fillers had less negative effect on paper strength compared to conventional fillers. It was believed that for spray dried fillers, fiber-filler and filler-filler bonding strength were increased compared to conventional fillers because the filler aggregates/particles were covered with a thin layer starch. If the filler aggregates with sphere shapes were broken into small pieces, more individual filler particles would be exposed to fibers. The breaking up of the starch coated filler in water might cause positive or negative effects on paper strength, depending on how starch is coated on fillers. If most of newly generated small filler

aggregates and individual filler particles were well coated by starch, the paper strength would increase with the decrease of particle size. On the contrary, if the newly generated small filler aggregates were not well coated by starch (i.e. only the original big filler aggregates were coated by starch), the paper strength would decrease with the decrease of particle size. In order to test this assumption, spray dried fillers with and without crosslinkers were used to make handsheets for strength test.

The tensile results in Figure 7.4 indicate that the spray dried fillers with crosslinkers did not demonstrate any benefit for strength improvement. On the contrary, for a given filler dosage, the tensile index of handsheets with normal spray dried fillers were all higher than that of handsheets with crosslinker-sprayed fillers. It means the breaking up of the spray dried filler has little effect on paper strength. It is suggested that although the starch-coated fillers are likely to break up in water, the smaller size filler particles broken from the big aggregates are still coated well by starch. Therefore, the size stability of starch-coated filler in water is not a big concern for practical applications.

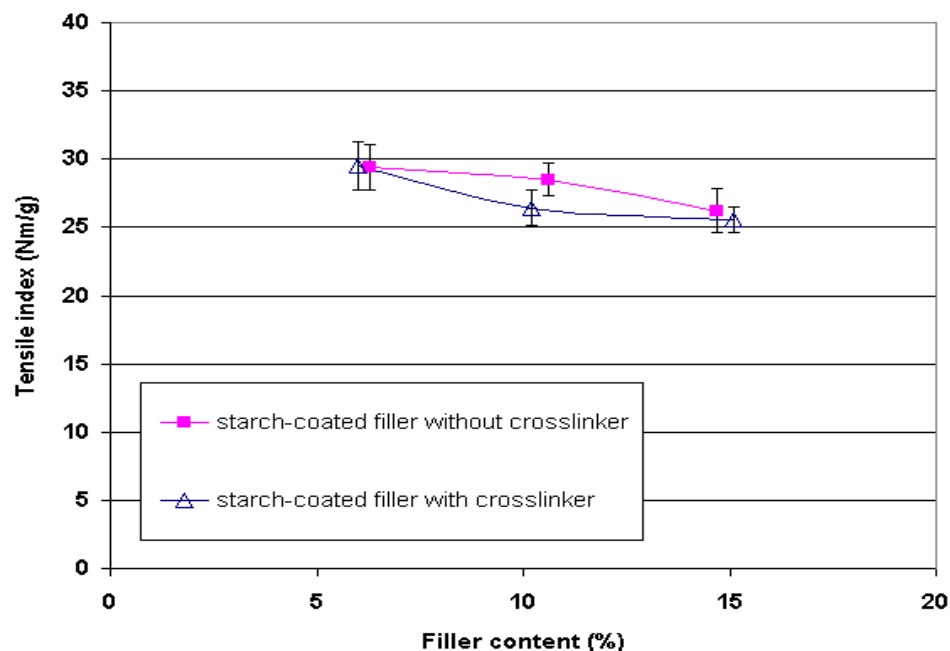


Figure 7.4 Tensile index of handsheets with different types of fillers.

7.4 Conclusions

- In aqueous solutions, the spray dried starch-coated fillers were likely to break into smaller-sized pieces;
- The addition of crosslinkers could significantly improve the rewetting stability of spray dried fillers, i.e. preventing the breaking up of filler particles;
- The addition of crosslinkers for stabilizing starch coating layer has little effect on the strength of handsheets, which means that the breaking up of the starch-coated fillers in water is not a serious concern for practical applications.

CHAPTER 8

STARCH NANOPARTICLE FORMATION VIA REACTIVE EXTRUSION AND RELATED MECHANISM STUDY

Abstract

In this chapter, starch nanoparticles were prepared by using a reactive extrusion method. The mechanism of starch nanoparticle formation during extrusion was investigated. The effects of extrusion conditions, including temperatures (50~100°C), screw speed, torque, starch water content and crosslinker addition, on particle size were studied. The results indicate that after extrusion at 100°C without crosslinkers, starch particles with a size of 300 nm could be obtained. With the addition of appropriate crosslinkers (glyoxal), the starch particle size could be reduced to approximately 160 nm, even at a lower extrusion temperature of 75°C. The addition of crosslinkers (glyoxal) could significantly increase the shear force (torque), and therefore facilitate the reduction of particle size. Compared to the original starch granules, the crystallinity of extruded starch nanoparticles is lower as indicated by x-ray pattern. The extruded starch nanoparticle suspensions at high solid content (9%) had a much lower viscosity than the cooked starch at a low solid content (3%).

8.1 Introduction

As a typical biodegradable natural polymer, starch is a good candidate for nanocrystals/nanoparticles. Starch nanoparticles or nanocrystals have many potential applications in various aspects, such as plastic fillers (Angellier, Molina-Boisseau et al. 2005; Angellier, Putaux et al. 2005; Kristo & Biliaderis 2007), food additives, drug carriers (Simi & Emilia Abraham 2007), implant materials (Thielemans, Belgacem et al. 2006), biodegradable composites (Chen, Wei et al. 2008), coating binders (Bloembergen, McLennan et al. 2008), adhesives (Bloembergen, Kappen et al. 2005) and so on. Starch nanoparticles also have a great potential for use in papermaking wet end, surface sizing, coating and paperboard as an biodegradable adhesive for substitution of petroleum based adhesives. In addition, starch nanoparticles have many advantages over traditional cooked cationic starch or anionic starch, due to its unique properties such as low viscosity of the suspension even at very high solid concentrations (up to 30 wt%), and higher bonding strength (Bloembergen, Kappen et al. 2005; Bloembergen, McLennan et al. 2008).

Starch nanocrystals/nanoparticles can be prepared by three different ways, including acid or enzymatic hydrolysis, regeneration, and mechanical treatment (Le Corre, Bras et al. 2010). Acid hydrolysis is a typical way to generate starch nanocrystals, but the method of acid hydrolysis is difficult for practical applications due to its low yield, long treatment period, and use of acid. Nanosized starch particles can be regenerated by precipitating starch solutions with some organic solvents. Starch nanoparticles can also be prepared by

processing starch granules with mechanical and thermal treatment, such as high pressure homogenization (Liu, Wu et al. 2009; Shi, Li et al. 2011), and reactive extrusion (Giezen, Jongboom et al. 2000). The reactive extrusion method is a high yield and environmentally friendly method for producing starch nanoparticles. Basically, the premixed starch and plasticizer were loaded into a twin screw extruder, and reversible crosslinkers, such as glyoxal, was added. They claimed that crosslinking via chemical bond formation during the mechanical treatment is an essential step. After the mechanical treatment, partial or even complete cleavage of the crosslinks is realized. However, the mechanism of starch nanoparticle formation during extrusion was not clearly reported.

During extrusion, starches are subjected to relatively high pressure, high temperature and high shear force, resulting in significant structural changes, including gelatinization, melting, and fragmentation (Lai & Kokini 1991). The hydrogen bonds between linear amylose and branched-chain amylopectin can be broken under high shear force and high temperatures (Lai & Kokini 1991). It was reported that the molecular weight (M_w) decreased exponentially when the specific mechanical energy input increased (Xie, Yu et al. 2006). However, no starch particle size measurement was involved in these studies.

The objective of this chapter is to investigate the mechanism of starch nanoparticle formation via reactive extrusion. The effects of extrusion conditions, such as temperatures, screw speed, crosslinker and water content on starch extrusion process and starch particle size were systematically studied. The transitional properties of starch

particles, including morphology, zeta potential, crystallinity structure and rheology properties, at different size levels were also characterized.

8.2 Experiments

8.2.1 Materials

Native corn starch (B200) was provided by Grain Process (Muscatine, Iowa USA). Glycerol (99% pure) and glyoxal (40% aqueous solution) were purchased from Aldrich USA, and were used as the plasticizer and the crosslinker respectively.

8.2.2 Starch nanoparticle preparation

The starch nanoparticles were prepared by using the method described in the patent (Giezen, Jongboom et al. 2000) with minor modifications. Giezen used a continuous feeding extruder with 9 heat zones. In our study, a batch feeding extruder with one single heat zone was used. The process is summarized in Figure 8.1. Native corn starch granules were premixed with water and glycerol using a lab blender at a weight ratio of 100: 22: 23 (starch: water: glycerol). The well mixed mixture was put into a plastic bag, and stored in a refrigerator at around 2°C for 24 hours. A co-rotating twin-screw extruder (HAAKE Minilab) was used to extrude the starch premix. The screw speed range is 100-360 rpm. Amount of starch used for each batch is 5 grams. 10% glyoxal aqueous solution was added in the starch premix or at the chemical addition point of the extruder (the

downstream hopper) at a dosage level of 0.5-3% pure glyoxal (based on the dry starch amount). As a dialdehyde compound, glyoxal has two carbonyl groups on its molecules they can react with hydroxyl groups in starch molecules (Yang, Dou et al. 2005). Acetalization reaction can occur, i.e. acetal bonds are formed between the hydroxyl groups and aldehydes. Heat is required to initiate reactions and achieve curing.

The extrusion was conducted within 55-110°C. The starch samples could be directly flushed out through a die, or cycle inside for a longer residence time. The torque was monitored and recorded by a reading screen, and the peak value was reported and used for comparison. In Giezen's patent, the extrudates were ground and sieved, followed by dispersing the starch particles in water. In our study, no grinding and sieving were conducted, and the starch extrudates were simply cut into small pieces (around 0.3 cm) and immersed in water for 1 hour. The starch pieces were further broken by an Ultra Turrax homogenizer (IKA T18 BASIC) at a speed of 16000 rpm for 30 minutes, producing starch particle suspensions.

The prepared starch particle suspension was diluted, and used for particle size measurement and rheology tests. Part of suspension was freeze dried, and the dried powder was used for determining starch crystalline structure.

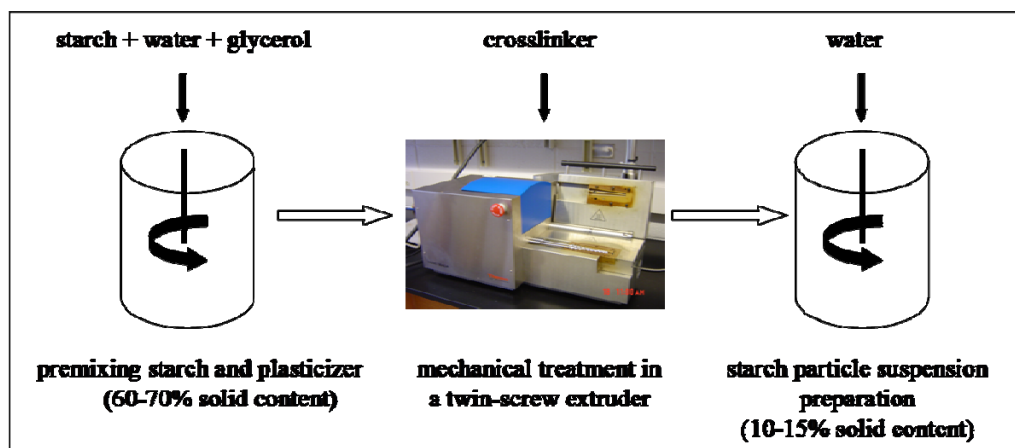


Figure 8.1 Process of starch nanoparticle preparation.

8.2.3 Characterization

The starch extrudates were observed and photographed under an optical microscopy. The particle size and zeta potential of the prepared starch particles were measured using a Malvern Zetasizer 3000. The viscosity of prepared starch particle suspension was measured using an MCR 300 (Anton Paar) rheometer with a couette geometry. The morphology of starch particles was observed using a scanning electron microscopy (SEM LEO 1530). The crystalline structure of freeze dried starch powders was determined using a wide angle X-ray diffractometer (PANalytical X'Pert PRO) with Cu K α radiation ($\lambda = 0.154$ nm). The scanning was conducted at 40kV with a rate of 0.5° per minute. The diffraction data from 5 to 35° were collected. ^{13}C CP/MAS solid state NMR was also used to determine the fine structure of the starch powders.

8.3 Results and Discussion

8.3.1 Appearance of extruded starch rods

Premixed starch samples (starch with plasticizer) were loaded into the extruder and processed under different conditions, including temperatures, screw speed, crosslinker dosage and starch water content. The appearance of extruded starch rods is shown in Figure 8.2. The diameter of the rods is around 2-3 mm. Starch rods with smooth surface were obtained when no crosslinker was added. The color of rods changed from white to translucent with the increase of extrusion temperature (Figure 8.2 a, b, c). When crosslinker (2% glyoxal) was added, the surface of the extruded rods became rough (Figure 8.2 d, e, f) even at a low extrusion temperature (60°C), indicating some pattern of damage which might be attributed to high shear force during extrusion. This will be further discussed later.

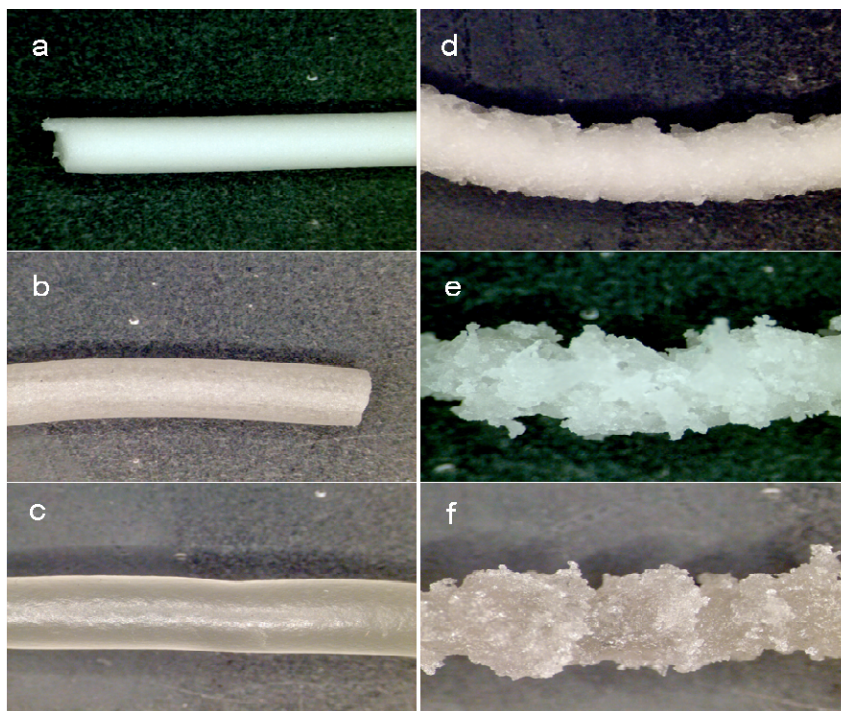


Figure 8.2 Extruded starch rods without glyoxal (a: 70°C; b: 90°C; c: 100°C) and with 2% glyoxal (d: 60°C; e: 70°C; f: 90°C).

Besides glyoxal, other crosslinkers, such as polyamide–epichlorohydrin (PAE), ammonium zirconium carbonate (AZC) and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) were also tried for starch extrusion. Unlike the extrudates with glyoxal, the extruded starch rods with other crosslinkers all demonstrated a smooth surface (Figure 8.3 b, c, d). The appearance of extruded rods is dependent on the torque induced during extrusion. During the extrusion with glyoxal, a torque higher than 200 Ncm was induced, resulting in a rough rod surface. However, for extrusion with other crosslinkers or without crosslinker, a low torque (less than 130 Ncm) was induced, and the extruded rods show a smooth surface.

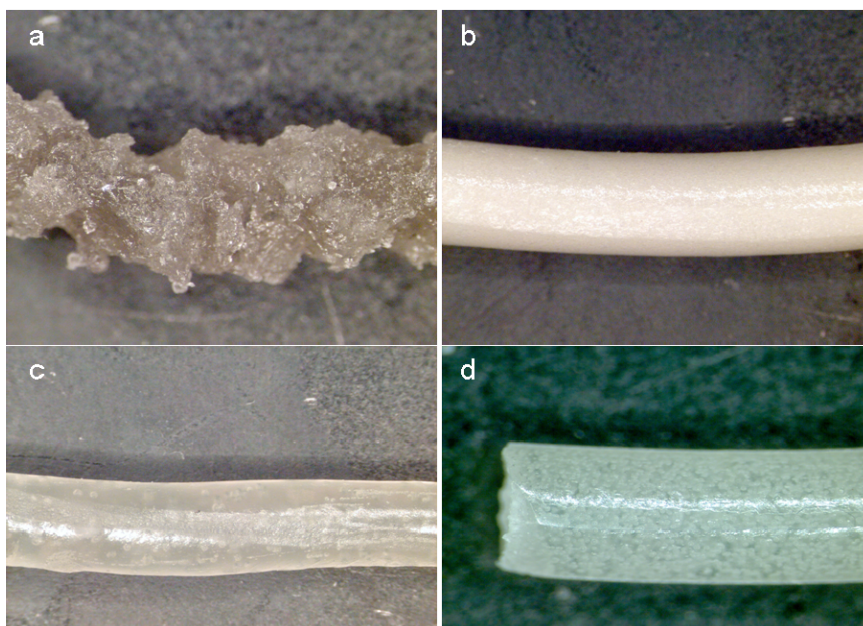


Figure 8.3 Starch extrudates with different crosslinkers (90°C, 300rpm) (a: 2% gloxal ; b: 2% PAE; c: 2% AZC; d: 1% Na₂B₄O₇).

8.3.2 Morphology and particle size distribution of extruded starch particles

The extruded starch rods were cut into small pieces and immersed in water. After 30-minute high speed stirring, a well dispersed starch particle suspension was obtained. The size and morphology of starch particles were characterized with SEM. The morphology of original starch particles is shown in Figure 8.4 a. It can be seen that most of the granules are spherical, and the average size is around 10-15 μm . After extrusion at 55°C without crosslinker, the average starch particle size was reduced to 2-5 μm (Figure 8.4 b). After extrusion at 85°C without crosslinker, the average starch particle size further reduced to 1-2 μm (Figure 8.4 c). On contrary, at the same extrusion temperature (85°C),

when 2% glyoxal was added during extrusion, nano sized starch particles with a size around 160 nm were obtained (Figure 8.4 d).

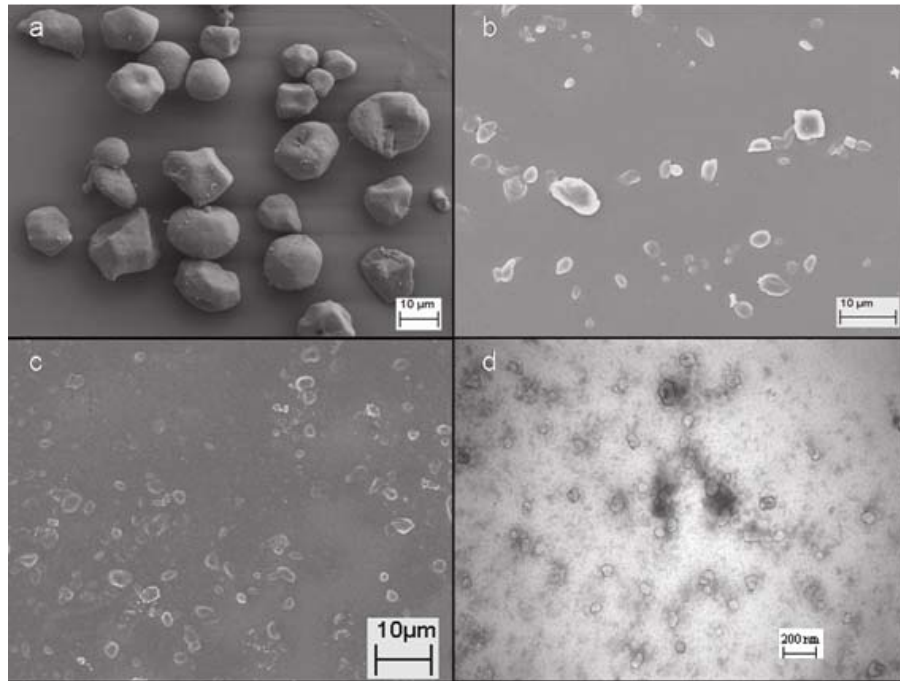


Figure 8.4 SEM images of starch particles (a: original starch granules; b: extruded starch at 55°C without crosslinker at 200rpm; c: extruded starch at 85°C without crosslinker at 200rpm; d: extruded starch at 85°C with 2% glyoxal at 200rpm). Scale bar for a, b, and c is 10 μm and for d is 200 nm.

SEM images can provide visual comparison of starch particles at different size levels. In order to obtain a statistical result, the average particle size and number intensity distribution of the particle size were determined using light scattering.

For extrusion without crosslinkers, the starch particle size decreased with the increase of extrusion temperature, as shown in Figure 8.5. The size distribution also changed with the temperature. At a low extrusion temperature, for example 55°C, the size distribution is

very broad, at a range of 500~5000 nm. At a higher extrusion temperature of 90°C or above, a much narrower size distribution was presented.

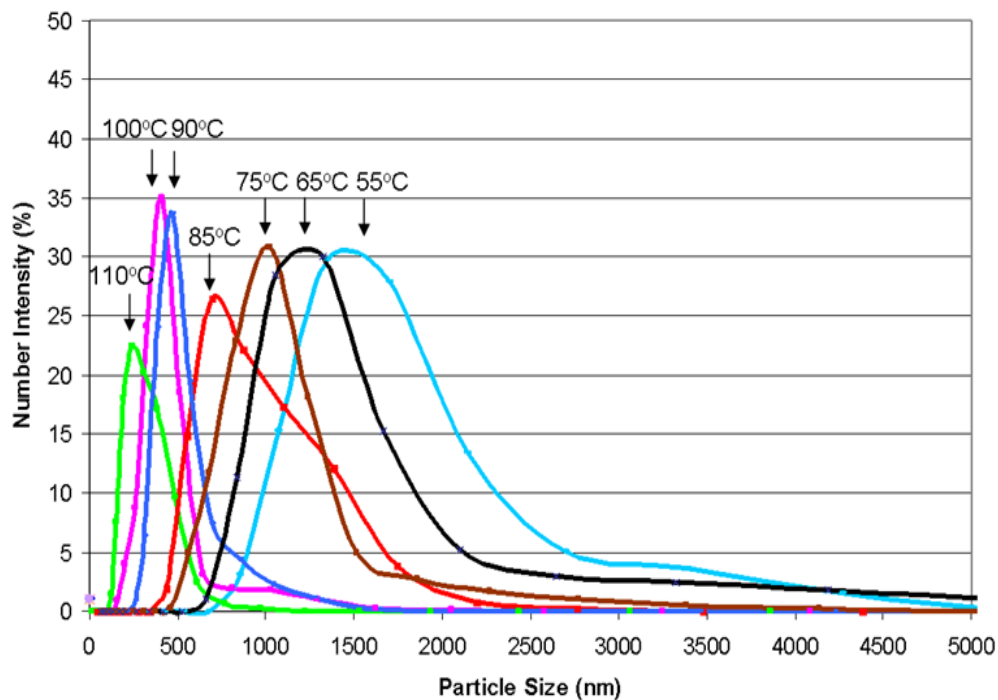


Figure 8.5 Starch particle size distributions for extruded starch particles at different temperatures measured in deionized water (no crosslinker, 300rpm).

The size change of extruded starch particles with 2% glyoxal is shown in Figure 8.6. With the increase of extrusion temperature, the particle size decreased sharply initially, and then kept at a low level around 100-200 nm at 75-100°C. At low temperatures (55 and 65°C), the size distribution was broad. At higher extrusion temperatures (>70°C), a narrower size distribution could be achieved.

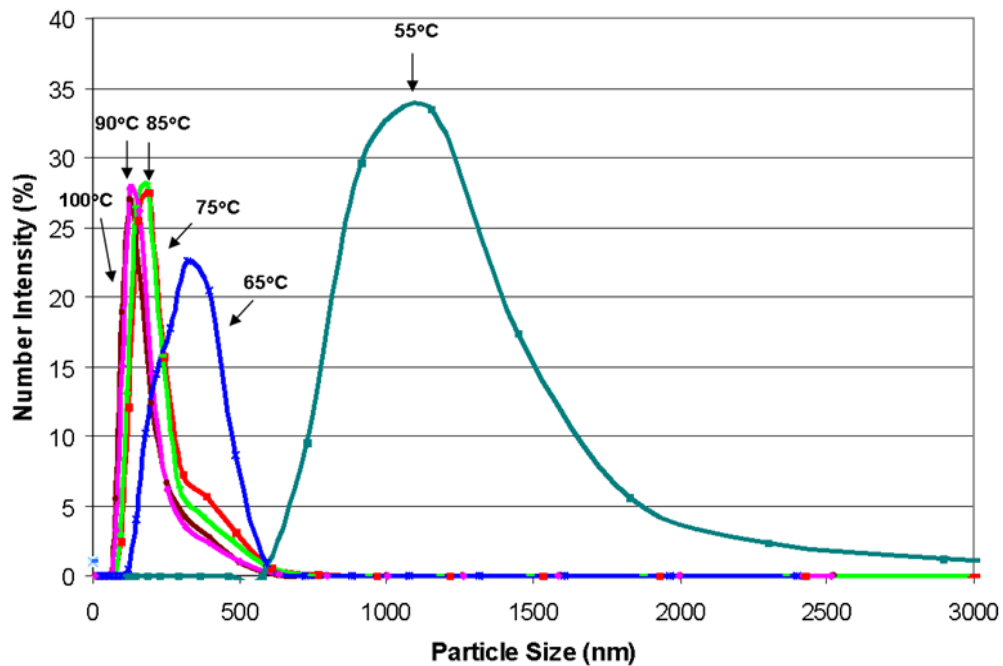


Figure 8.6 Starch particle size distributions for extruded starch at different temperatures measured in deionized water (2% glyoxal, 300rpm).

At the same extrusion temperature, the size of starch particles extruded with crosslinker (2% glyoxal) is much smaller than that without crosslinker. For example, at 65°C, the average size of starch particles without crosslinker is around 1300 nm, while the average size of starch extruded with 2% glyoxal is about 300 nm. These results suggest that the crosslinker (glyoxal) can facilitate the reduction of particle size during extrusion, which agrees well with literature (Giezen, Jongboom et al. 2000). The mechanism of how the crosslinker addition can reduce the particle size and the size distribution will be discussed later.

8.3.3 Mechanism of starch nanoparticle formation

The process of starch nanoparticle preparation includes two main steps: extrusion and post breaking-up in water. The latter is a simple treatment of high speed stirring. According to the preliminary test, the raw starch granules could only be broken into smaller particles of 3-5 μm even after 1 hour high speed stirring with our Turrax homogenizer. Therefore, we believe that the main contribution to the generation of starch nanoparticles is from extrusion.

During extrusion, starches are subjected to high temperature and high shear force. Essentially, starch gelatinization, melting and fragmentation occur, resulting in the decrease of starch particle size. Klingler et al. proposed that both the thermal and mechanical energy applied to starch during extrusion may cause the breakdown of covalent bonds and hydrogen bonds between starch molecules (Klingler, Meuser et al. 1986). Colonna et al. found that the average molecular weight of amylose and amylopectin significantly decreased after extrusion (Colonna, Doublier et al. 1984). With the breakdown of those bonds, starch granules might be easily torn apart into smaller particles, even to nanosize. In this study, the contributions of heat, shear and chemicals were identified by investigating starch extrusion at different combinations of processing conditions.

The extrusion temperature or thermal energy usually has strong impact on polymer morphology, crystallinity and chemical compositions. To study the extrusion temperature

effects on the starch particle size, the extrusions at a fixed screw speed of 300 rpm with different temperatures were conducted. For the extrusion without crosslinkers, the starch particle size decreased with the increase of extrusion temperatures (Figure 8.7 the upper solid line). However, the torque during extrusion was decreased with the increase of temperatures. This is because at higher temperatures, a higher extent of starch softening and melting requires less energy (shear force) to push starch through the extruder. Therefore, a decreased torque was observed. On the other hand, the highly softened and melted starch granules are easier to be torn apart into smaller particles even at a small torque of 120 Ncm. That means the reduction of starch size with temperature increase is likely due to heat effect, i.e. thermal energy effect.

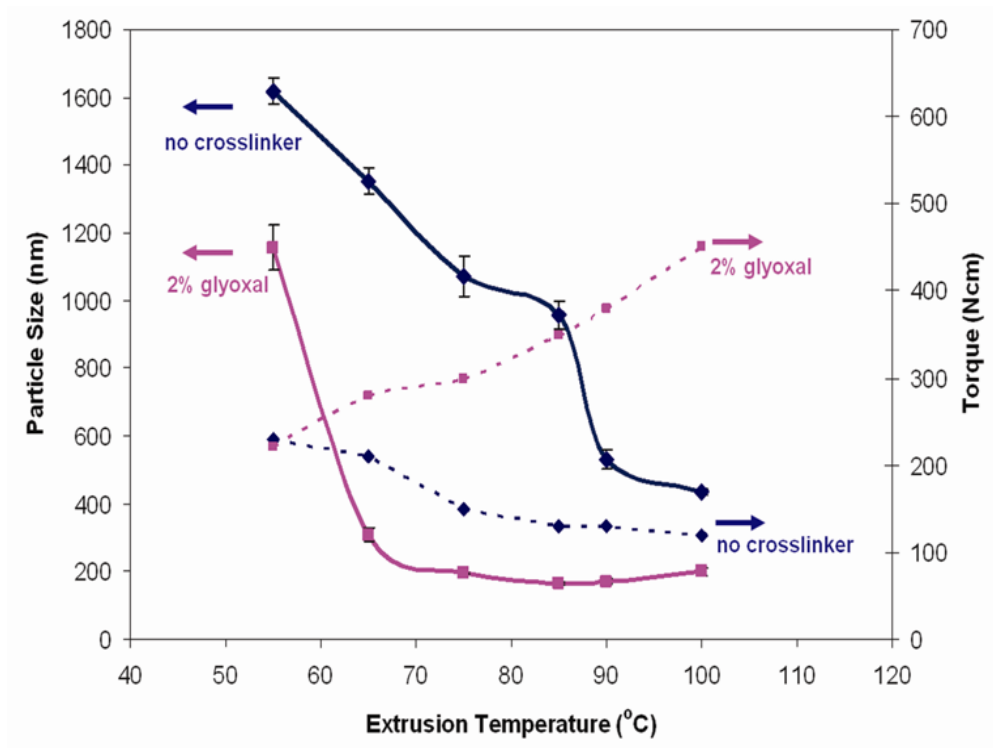


Figure 8.7 Particle size (solid lines) and torque values (dash lines) at different extrusion temperatures.

When crosslinker (2% glyoxal) was added during extrusion, the starch particle size was sharply decreased when the temperatures increased from 55 to 75°C. A further increase of temperatures only lowered the particle size slightly. It is interesting to note that the dependence of torque on the temperature is totally different for the starch systems with and without crosslinkers. As shown in Figure 8.7 (the upper dash lines), the torque increased with the temperature when crosslinker was added, but it decreased for the system without crosslinker. Generally speaking, the higher temperature will result in a decrease of the viscosity for melted starch so a decrease in torque should be observed. However, for the extrusion of starch in presence of crosslinker (glyoxal), the crosslinked starch network is formed, which has a negative impact on the softening and melting of starch. As a result, a higher torque is needed during extrusion, and a smaller starch particle size can be reached, compared to extrusion without a crosslinker. Furthermore, raising temperature can result in an increase of the crosslinking rate, and an increase in torque.

In order to study the effect of mechanical energy, the extrusion temperature was fixed and the extrusion at different screw speeds were conducted, which corresponds to the different shear forces applied. It was shown in Figure 8.8 (dash lines) that for a given temperature regardless of using crosslinker or not, the faster the screw speed, the higher the torque. Furthermore, a much higher torque could be achieved when crosslinker (glyoxal) was added. For example, at a screw speed of 360 rpm, the torque for the extrusion with 2% glyoxal at 75°C was about 390 Ncm, while a much lower torque (around 140 Ncm) was measured for the extrusion without crosslinker. As we discussed before, the high torque was attributed to the crosslinking effect during extrusion.

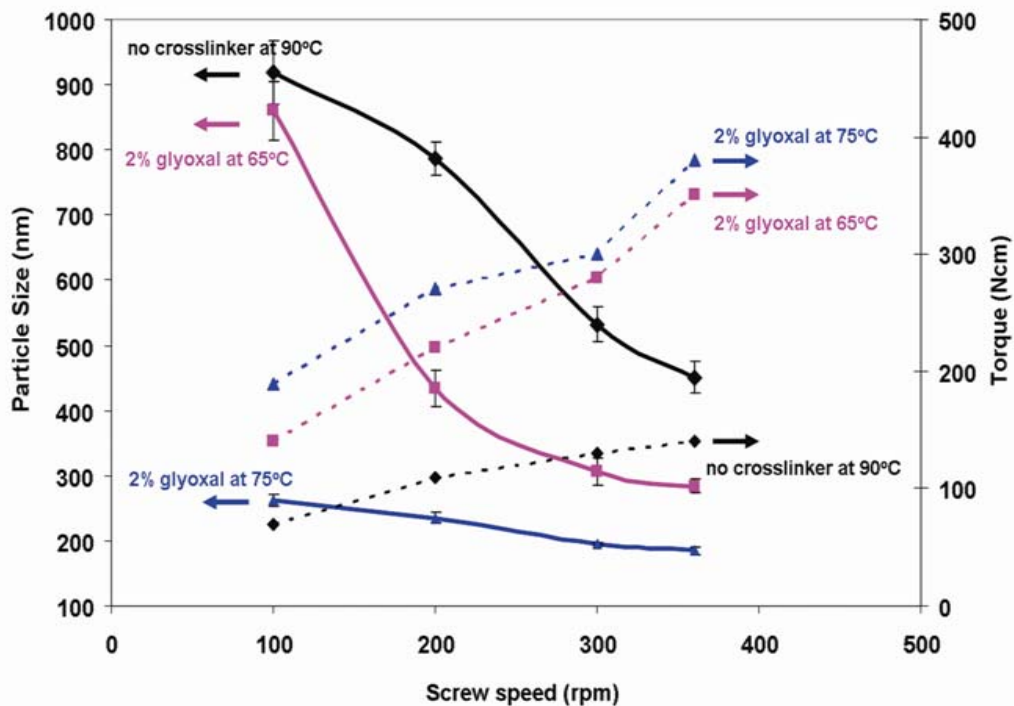


Figure 8.8 Particle size (solid lines) and torque values (dash lines) at different extrusion screw speeds.

Figure 8.8 (solid lines) shows that at a given extrusion temperature, the starch particle size was decreased with the increase of screw speed, i.e. torque values, which suggests that the shear force is critical for the reduction of starch particle size during extrusion. It has been known that fragmentation of starch during extrusion is attributed to the specific mechanical energy (SME) (Klingler, Meuser et al. 1986; Seker & Hanna 2005). Furthermore, it can be seen in Figure 8.8 (solid lines) that even at a low extrusion temperature (65°C), the particle size of extruded starch with crosslinkers (2% glyoxal) is much smaller than that of the starch extruded without crosslinker at a high temperature of 90°C. This is mainly because a higher torque was applied during extrusion with crosslinker.

Figure 8.8 also shows that for extrusion with 2% glyoxal at a low temperature (65°C), starch particle size decreased sharply with the increase of torque. This result suggests that, at a low temperatures, the softening and melting of starch granules are limited, and the resultant particle size is highly dependent on the mechanical energy induced. However, at higher temperatures (75°C), the particle size was reduced to a low level and almost kept constant at different torques. During the extrusion at high temperatures, both heat and shear force are important. First of all, a high extent of starch softening and melting could be realized, and it is much easier to tear starch granules apart into smaller particles. At the same time, a crosslinked starch network was formed due to the induction of glyoxal. When crosslinked starch was going through the screws, a high torque (>200 Ncm) was reached, even at a low screw speed (100 rpm). At such a high torque, the softened, melted and crosslinked starch could be easy to be torn apart into nanosized particles. However, a further increase of torque could only slightly decrease the particle size.

Starch extrusion with different crosslinker (glyoxal) dosages was also conducted, and the corresponding torque and size are summarized in Figure 8.9. The higher the crosslinker dosage, the higher the torque, and the lower the resultant particle size. This result further proves that the addition of crosslinkers could increase the shear force during extrusion, which facilitates the reduction of starch particle size.

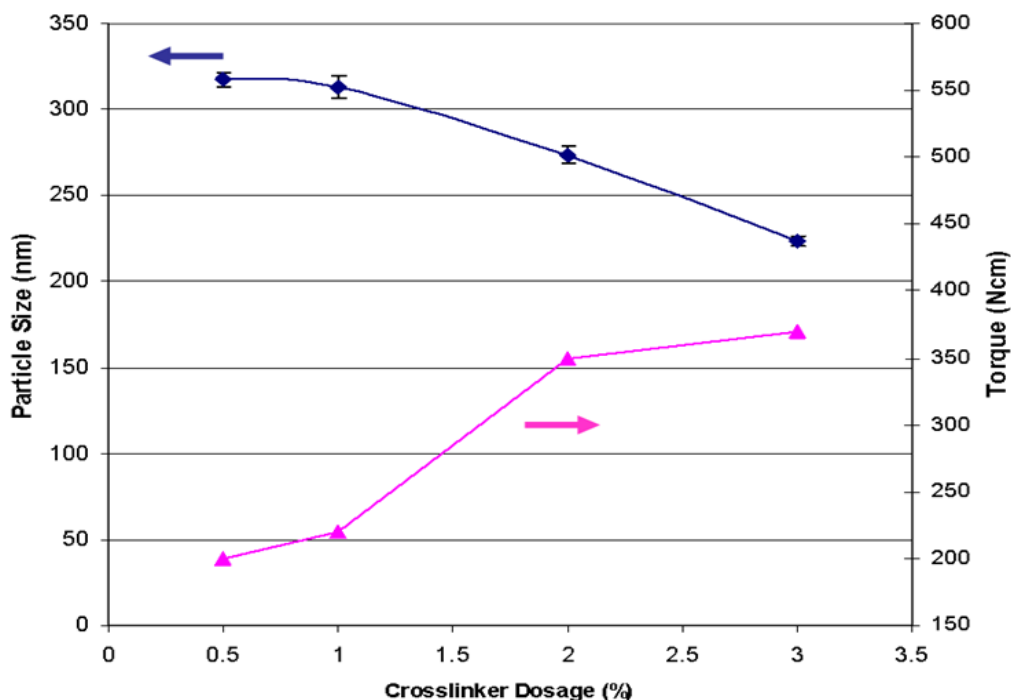


Figure 8.9 Effect of crosslinker (glyoxal) dosages on particle size and torque (at 90°C and 300 rpm).

The effect of crosslinker types on particle size was also investigated. It is shown in Figure 8.10 that the addition of crosslinker could further reduce the size of starch particles, particularly for the extrusion with glyoxal. Essentially, the size reduction for extrusion with crosslinkers is attributed to the increased torque caused by crosslinking. For extrusion with glyoxal, the torque is very high (>350Ncm) so that a smaller particle size less than 200 nm was reached. On contrary, the torque for the extrusion with AZC, PAE and $\text{Na}_2\text{B}_4\text{O}_7$ was close to or even smaller than that without crosslinker. Therefore there is no significantly size reduction for extruded starch particles. These result suggest that only certain crosslinking reactions could significantly increase the torque during extrusion, and facilitate the reduction of particle size.

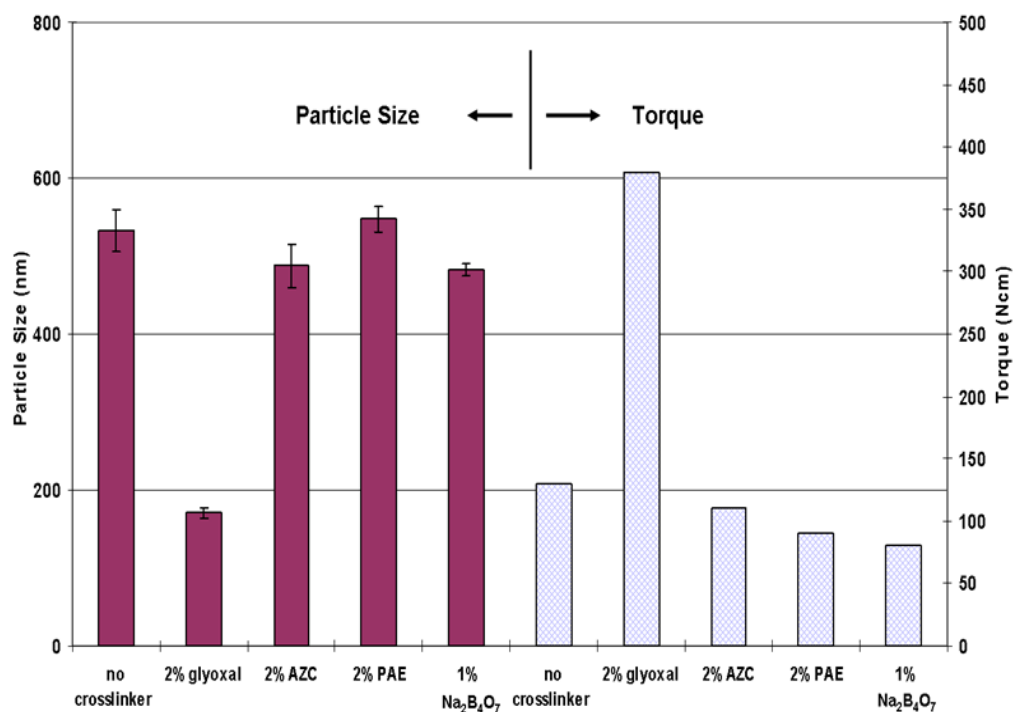


Figure 8.10 Particle size and torque for extrusion with different crosslinkers (90°C, 300 rpm).

Different residence time of starch in the extruder was chosen, and their effect on starch particle size was compared (Figure 8.11). Basically, the longer the residence time, the lower the particle size. But the difference is not significant.

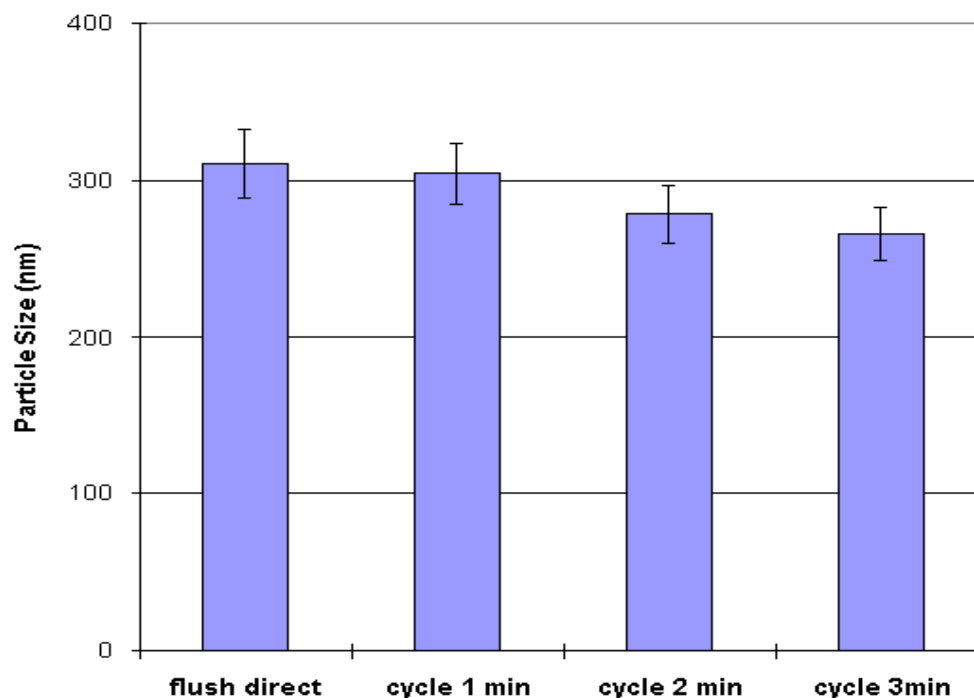


Figure 8.11 Particle size of extruded starch with different residence time (1% glyoxal, 90°C, 300rpm).

Starch softening and melting occurs at high temperatures. The effect of starch softening and melting on particle size of extruded starch is complicated. Under high shear force, softened and melted starch can be broken into smaller particles easily. On the other hand, the softened and melted starch is easier to be transported through the channel of extruder by the screws, resulting in a low torque (shear force) during extrusion. The degree of softening and melting is highly dependent on water contents of starch. Figure 8.12 shows the change of particle size and torque at different water contents. For extrusion without crosslinker, as expected, the higher the water content, the lower the torque. However, it was found that, although the torque decreased with the increase of the water content, the actual particle size was decreased. The reduction of size for this case is mainly attributed

to enhanced starch swelling and softening at the higher water content, though the torque values decreased. For the extrusion with crosslinkers (2% glyoxal), the torque decreased with the increase of water content, and the particle size was increased. The results suggest that, for the extrusion with crosslinker, the effect of torque reduction overtook the contribution of starch swelling and softening.

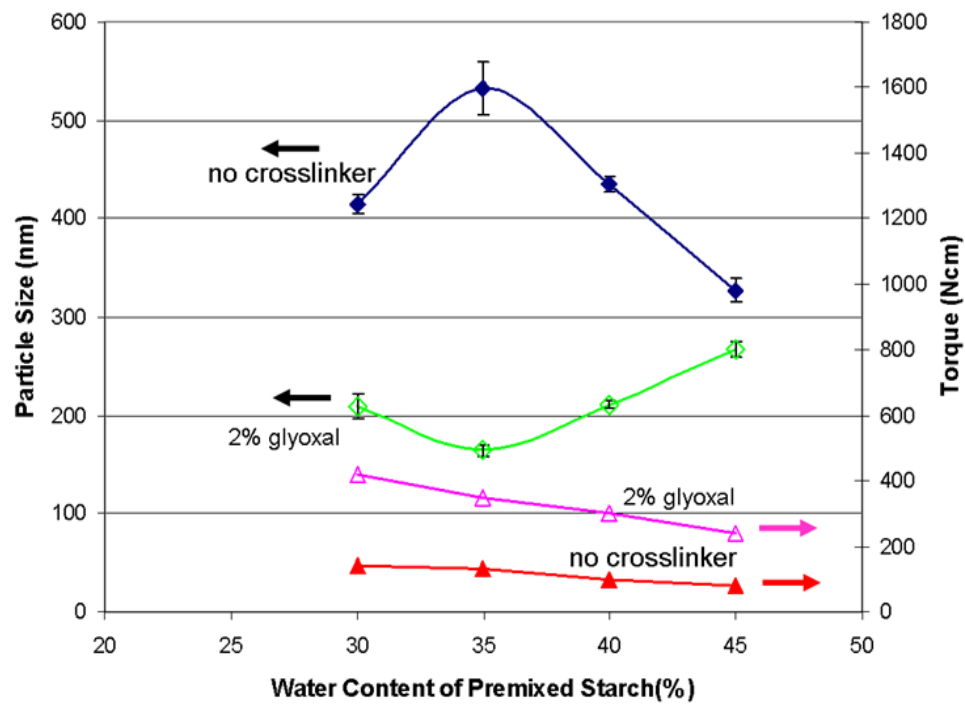


Figure 8.12 Particle size and torque for extrusion at different water contents (extrusion at 90°C, 300rpm).

8.3.4 Transitional properties of extruded starch particles

8.3.4.1 Zeta potential

The zeta potential of starch particles extruded at different temperatures was also measured (Figure 8.13). For starch extrusion with or without crosslinkers, the zeta potential increased (the absolute values decreased) with the extrusion temperature. It was also shown from previous section that the particle size decreased with the extrusion temperatures. These results suggested that, for extruded starch particles, the smaller the particle size, the higher the zeta potential. In contrast, Liu reported that for high pressure homogenization treatments, the smaller the particle size, the lower the zeta potential (Liu, Wu et al. 2009). They believed that the high pressure homogenization is a pure physical tear-apart process which releases more free hydroxyl groups on starch particle surface when particle size is decreased. However, extrusion conducted in this study is a complicated process including starch gelatinization, melting, fragmentation or even crosslinking. During the process of fragmentation (i.e. tear-apart), melting would also occur, and the released free hydroxyl groups might form hydroxyl bonds again at particle surface, resulting a higher zeta potential (smaller absolute values).

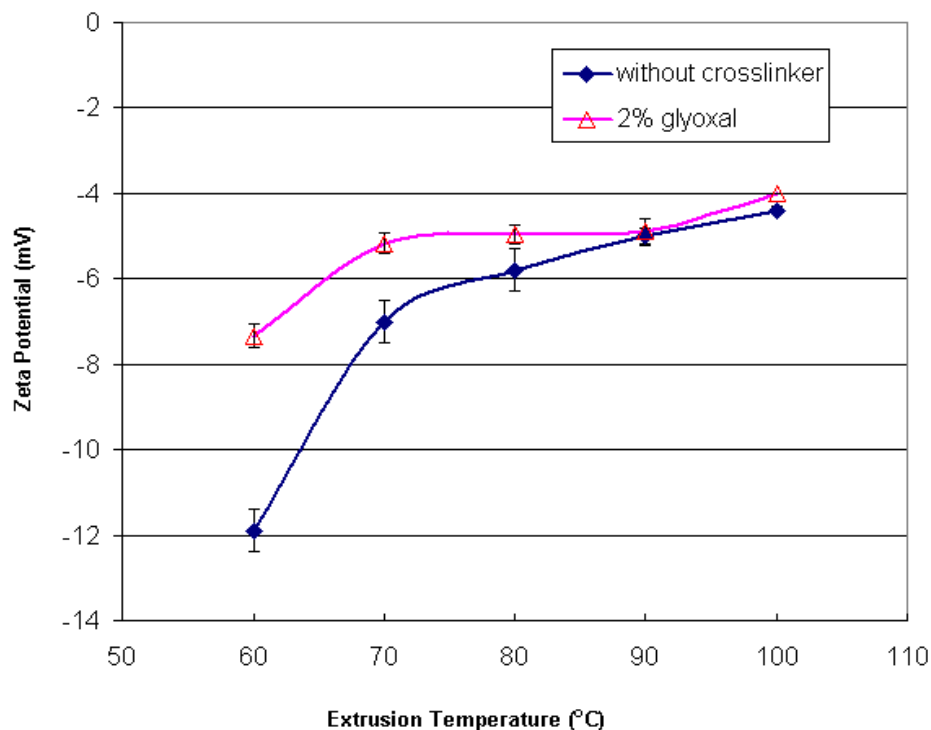


Figure 8.13 Zeta potential of starch particles extruded at different temperatures (extrusion at 360rpm).

8.3.4.2 Crystal structure change

In order to investigate the effect of extrusion on starch crystal structure, x-ray patterns were determined for different starch samples. As a native cereal starch, the original corn starch granule has an A-type crystallinity, i.e. showing strong diffraction peaks at around 15° , 17° , 18° and 23° (Figure 8.14 a), which agrees with the literature (Zobel 1988; Bhatnagar & Hanna 1994a; Cheetham & Tao 1998b; Sívoli, Pérez et al. 2009). During the extrusion process, starch granules were exposed to high temperature and high shear force so that the particle size decreased. As a result, the crystalline structure would also change. Figure 8.14 shows, the diffraction peaks diminished or even disappeared for extruded starch particles (Figure 8.14 b,c,d). For the x-ray pattern of extruded 300 nm

starch (Figure 8.14 d), the peaks at 15° , 18° and 23° totally disappeared, and only a small peak at 17° exists after extrusion, which suggests that the extrusion, i.e. combination of heat and shear force, caused a significant change on starch crystal structures. Farhat et al. reported that the native starch lost its A type crystalline structure on extrusion, and the crystallinity of extruded starch is only 2-4% (Farhat, Mitchell et al. 1996). Liu et al. also reported that the degree of crystallinity of starch particles decreased with the reduction of particle size during high pressure homogenization treatment (Liu, Wu et al. 2009). They argued that both amorphous and crystalline part of starch granules were broken into much smaller particles under mechanical treatments.

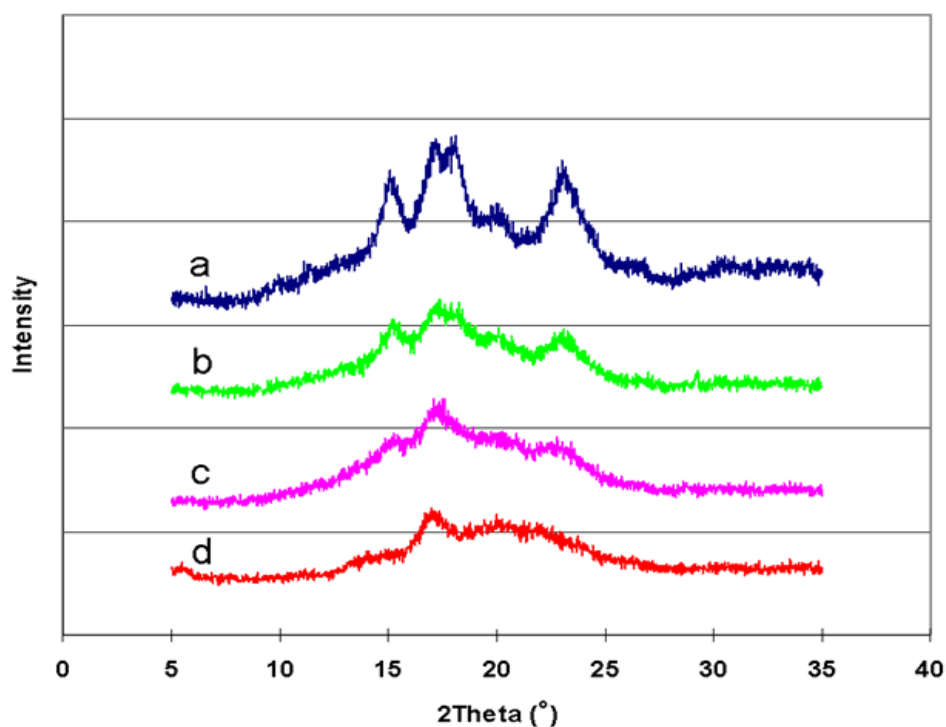


Figure 8.14 X-ray pattern of starch particles (a: raw starch granules; b: extruded starch without crosslinker (1 μm); c: extruded starch without crosslinker (600 nm); d: extruded starch without crosslinker (300 nm).

In order to obtain a good understanding on the crystalline structure change caused by extrusion, the effects of heat, shear force, and chemicals were identified respectively. In order to simulate the heating in extruders, premixed starch samples with or without crosslinkers were put in an oven at 90°C for 5 minutes. The x-ray pattern (Figure 8.15 b) shows that for starch without crosslinker, all peaks diminished compared to the pattern of raw starch granules (Figure 8.15 a), but the 4 peak pattern was still present. The result indicates that heat can partially reduce the crystallinity of starch. For starch with crosslinker (2% glyoxal), a similar results were obtained (Figure 8.15 c), which means the induction of glyoxal did not change the crystal structure of starch at heating.

For the extrusion treatment, when starch particle size was reduced to 300nm, the 3 peaks at 15°, 18° and 23° totally disappeared, and only a small peak at 17° exists (Figure 8.16 b,c). This means extrusion, i.e. heat and shear force, caused a much more significant change on starch crystalline, than heating alone. Therefore, shear force is an important factor affecting the starch crystalline structure. In addition, Figure 8.16 also shows that the x-ray patterns of extruded starch without or with crosslinker did not show significant difference. The results indicate that the crosslinking reaction itself did not change the crystal structure of starch, which agrees with previous results in literature. (Yoon, Chough et al. 2007; Sívoli, Pérez et al. 2009).

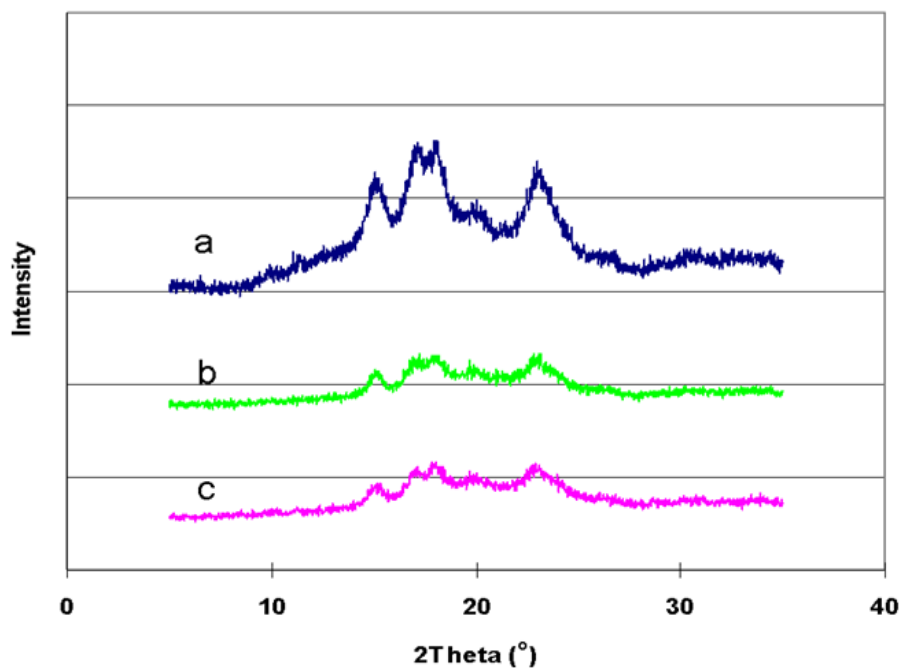


Figure 8.15 X-ray pattern of starch particles (a: starch granules without heating in oven; b: starch granules heated in oven; c: starch granules with 2% glyoxal heated in oven).

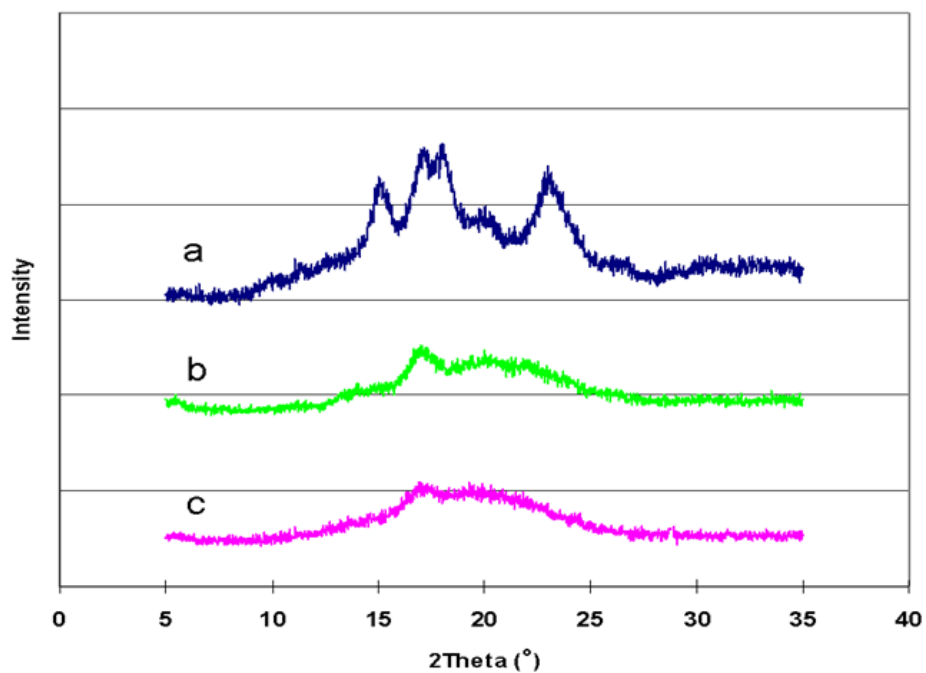


Figure 8.16 X-ray pattern of starch (a: starch granules; b: extruded starch without glyoxal (300nm); c: extruded starch with 2% glyoxal (300nm)).

Solid state NMR is a good technique for studying fine structure of polymers. Raw starch granule, 300nm starch particles extruded with and without crosslinkers were analyzed by solid state NMR, and the results are summarized in Figure 8.17 and Table 8.1. Some significant structure changes were demonstrated. For raw starch granules (Figure 8.17 a), there were 3 chemical shifts around 99.2-103ppm, representing C1. For 300nm starch particles extruded without crosslinker, two chemical shifts exists while only one chemical shift presents for 300nm starch particles extruded with crosslinker. For C6 position, two chemical shifts was shown for 300nm extruded starch particles, while there was only one chemical shift for raw starch granules. These NMR results indicated the change of fine structure occur during extrusion.

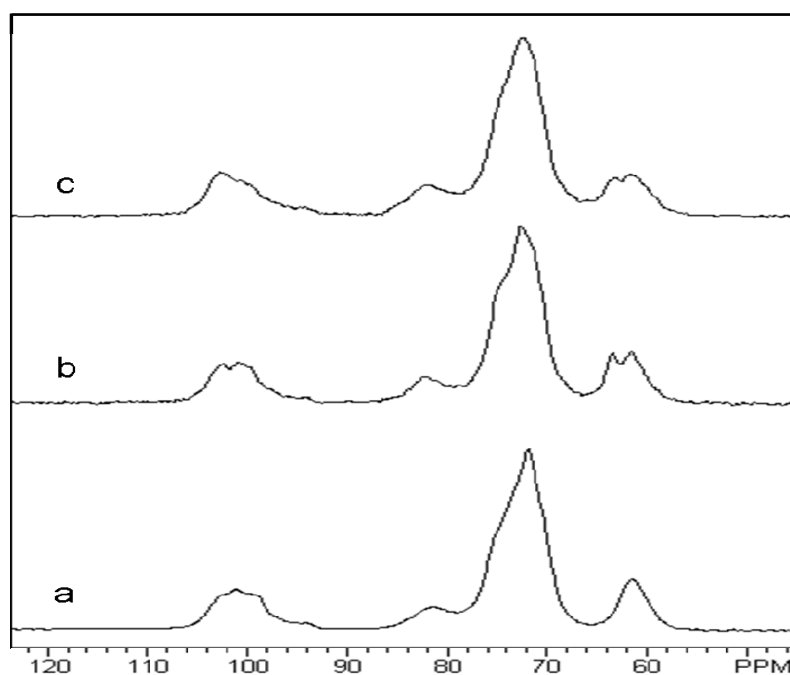


Figure 8.17 Solid state NMR profiles of different starch particles (a: starch granules; b: 300nm starch particles extruded without crosslinker; c: 300nm starch particles extruded with 2% glyoxal).

Table 8.1. ^{13}C chemical shifts and line-widths of corn starch for different treatments

Samples	C-1	C-4	C-2, C-3, C-5	C-6
raw starch particles	103.0 (552)* 101.4 (372) 99.2 (384)	81.7 (852)	72.2 (1333)	61.7 (840)
300nm starch particles (extruded without crosslinker)	102.7 (498.6) 100.8 (538.7)	82.3 (748.2)	72.7 (1117)	63.6 (319) 61.5 (478)
300nm starch particles (extruded with 2% glyoxal)	103 (1356)	82.3 (818)	72.8 (1197)	63.5 (299) 61.9 (578)

* The data in parentheses represent line-widths (Hz)

8.3.4.3 Rheological properties of starch nanoparticle suspensions

The viscosity of a particle suspension depends on many factors such as particle numbers, size, aggregation status and the interaction forces of particle-particle and particle-solvent. Highly swelled particles usually have a higher viscosity. Figure 8.18 shows that for a given shear rate, the viscosity significantly increased with the decrease of particle size, particularly when the size is reduced to 600 nm or lower. This is because, for a given mass concentration, the smaller the particle, the more particles in the solution, and the higher interaction between the particles, resulting in a higher viscosity of suspension. When starch particle size is higher than $1\mu\text{m}$, the viscosity of starch suspension kept

constant while changing shear rates. For starch particles with small size around 600 nm or lower, the suspension shows shear thinning phenomenon, i.e. viscosity decreased with the increase of shear rates.

The viscosity of starch nanoparticle suspension and cooked starch solution was also compared in Figure 8.18. At a high shear rate of 1000 s^{-1} , the viscosity of 300 nm starch particle suspension at 9% is lower by around 70% than that of cooked starch at a low solid content of 3%. A low viscosity at high solid contents is a great advantage of starch nanoparticles for industry applications.

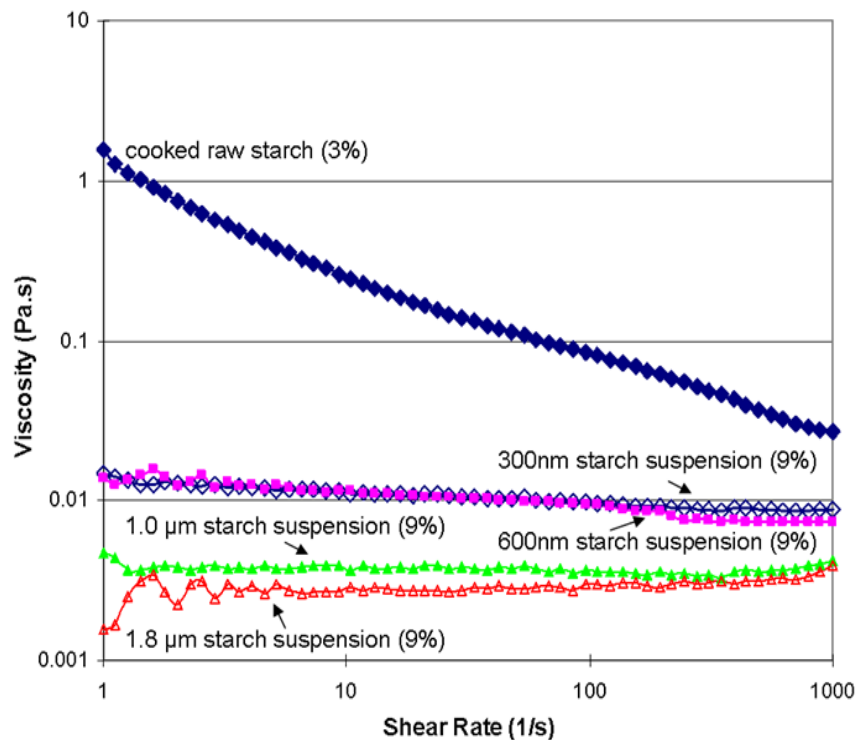


Figure 8.18 Viscosity of starch particle suspensions and the cooked starch at room temperature.

For raw starch granules, the viscosity of starch slurry normally experience a viscosity increase to a peak value and then a decrease phase during a typical cooking process. The viscosity of extruded nano starch suspension was also tracked for a cooking process. Figure 8.19 shows that the viscosity of starch solution decreased with the increase of temperature from 25 to 90°C and then become constant at a constant temperature step (95°C). The viscosity increased while the starch temperature decreased to 25°C. This viscosity profile indicates that the extruded nano starch can be considered as pre-cooked starch, and the cooking occurs during extrusion, though with a short period (~60 s).

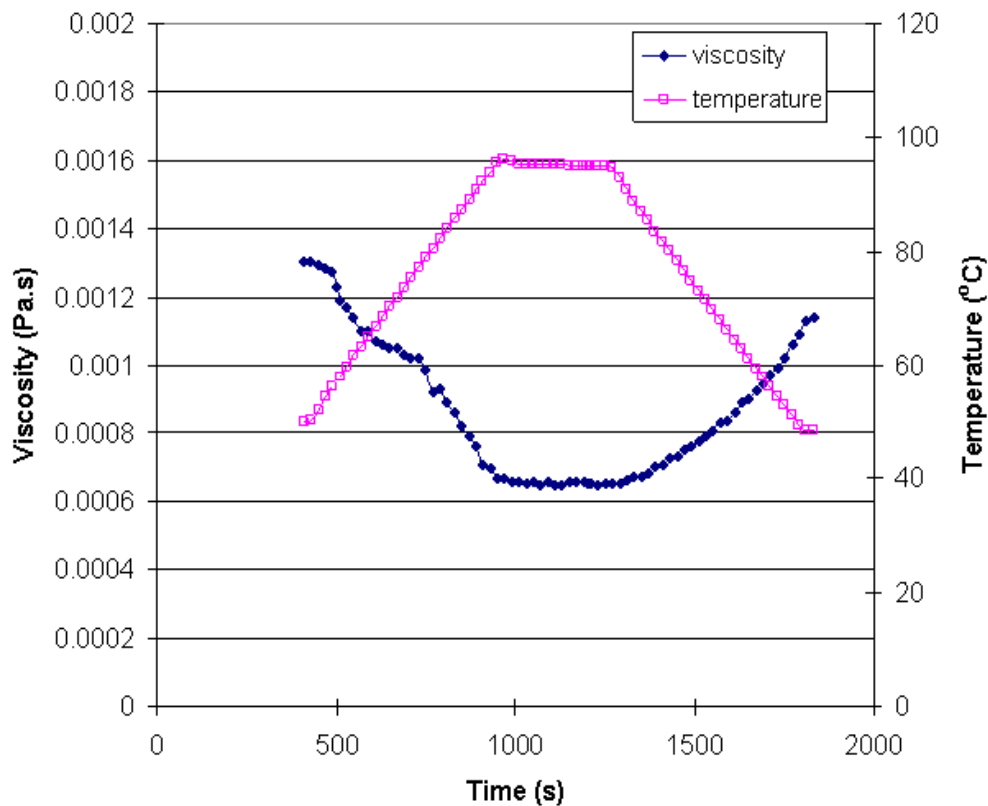


Figure 8.19 Viscosity profile of a starch nanoparticle suspension during cooking.

8.4 Conclusions

In this chapter, the mechanism of starch nanoparticle formation during extrusion was investigated. The effects of extrusion conditions, including temperatures (50~100°C), screw speed, torque, starch water content and crosslinker addition, on particle size were studied. The results indicate that after extrusion at 100°C without crosslinker, the starch particles with a size of 300 nm were obtained. The high temperature is an important factor for the reduction of starch particle size during the extrusion. With the addition of appropriate crosslinkers (glyoxal), the starch particle size could be reduced to approximately 160 nm, even at a lower extrusion temperature of 75°C. The addition of crosslinkers (glyoxal) could significantly increase the shear force (torque), and consequently facilitate the reduction of particle size. Compared to the original starch granules, the crystallinity of extruded starch nanoparticles was lower as indicated by the x-ray pattern. The extruded starch nanoparticle suspension at a high solid content of 9% had a much lower viscosity than that of the cooked starch at a low solid content of 3%.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Overall Conclusions

In this thesis work, fundamental understandings of starch crosslinking in both AZC-starch hydrogel network formation and starch nanoparticle formation during extrusion were obtained. As a new path for utilizing the low cost raw starch in papermaking, a novel method of cellulose fiber modification via starch grafting in the presence of a crosslinker was developed, and the improved paper properties and papermaking process were demonstrated. In addition, the size stability of starch-coated fillers in water was considerably improved by inducing crosslinkers during filler modification.

In the first part of this work, the self-crosslinking of ammonium zirconium carbonate (AZC) and its co-crosslinking with starch in aqueous solutions were investigated by using rheological measurements. The evolution of viscoelastic properties of the AZC solutions and the AZC-starch mixtures was characterized, and the crosslinking kinetics was determined. It was found that for both AZC self-crosslinking and AZC-starch co-crosslinking, the initial bond formation rate and the gel strength exhibit a power law scaling with the polymer and crosslinker concentration. The results indicate that the development of the crosslinking network is highly dependent on the AZC concentration, while the starch concentration is relatively unimportant. The temperature dependence of crosslinking described by an Arrhenius expression shows a good linearity. The activation

energy of AZC gelation is approximately 145.0-151.1 kJ/mol, while the activation energy of AZC-starch gelation is 139.3 kJ/mol. The CO₂ release rates show that AZC self-crosslinking and AZC-starch co-crosslinking have a similar link formation rate. The result indicates that the gel network development shows some delay following the link formation, i.e. CO₂ release.

Grafting starch onto cellulose fibers through the hydrogen bond formation among cellulose, starch, and AZC was conducted. The microscope images reveal that a reasonable amount of starch was grafted on fiber surface to form “starch fibrils”. The effects of grafting conditions, including pH, temperature, fiber consistency, AZC and starch dosage, and stirring speed, on the grafting yield were systematically investigated. Optimal reaction conditions for grafting yield were obtained (pH: 9; temperature: > 80°C; fiber consistency: 3%; starch dosage: 5%; AZC dosage: 2.5%). The soft starch hydrogel grafted on fiber surface was found to be sensitive to shear force. High shear forces should be avoided during post processing. It was also found that starch grafting treatment on fibers could significantly improve the water retention value of the fibers.

For unrefined and slightly refined fibers, the starch grafting treatment on fibers could significantly improve the strength properties of paper, including tensile, stiffness, and ZDT. Compared with the fibers at an industry refining level (420 ml CSF), the fibers with a much lower refining degree (600-700 ml CSF) but with grafted starches had faster water drainage and water removal rate in the press and drying process, equivalent or even higher paper strengths, including tensile, stiffness and ZDT. An optimal condition for the

starch grafting treatment was found to be 3% starch and 1-2% AZC based on fibers. Slight refining was found to be an effective way to disperse the starch grafted fibers in the dry pulp board with less damage to the grafted starch. The handsheets made of the repulped starch grafted fibers gave equivalent tensile strength and z direction tensile (ZDT), and higher stiffness, compared to the handsheets made of fibers at an industry refining level (~420 ml CSF).

By introducing crosslinkers during filler modification via starch coating, the size stability of the starch-coated fillers in water was considerably improved. Also, an interesting result was also found: the breaking-up of starch coated filler aggregates would have little effect on paper strength, which suggests that the size stability of starch-coated filler in water is not a serious concern for practical applications.

In the final part, the mechanism of starch nanoparticle formation during extrusion was investigated. The effects of extrusion conditions, including temperature (50~100°C), screw speed, torque, starch water content and crosslinker addition, on particle size were studied. The results indicate that after extrusion at 100°C without crosslinker, the starch particles with a size of 300 nm were obtained. With the addition of appropriate crosslinkers, the starch particle size could be reduced to approximately 160 nm, even at a lower extrusion temperature of 75°C. The temperature and torque are two important factors. The addition of crosslinkers (glyoxal) could significantly increase the shear force (torque), and consequently facilitate the reduction of particle size. Compared to the traditionally cooked starch at a low concentration of 3%, the starch nanoparticle suspension at a high concentration (9%) had a much lower viscosity.

Overall, the main objectives of this thesis work were to obtain improved understanding of starch crosslinking in the current processes and to develop new paths for utilizing starch in the paper industry or other industries. The modified fibers via starch grafting can be applied in both direct paper sheet preparation and dry pulp board preparation. Great benefits, including saved fiber refining and dewatering energies and improved paper strength, can be provided for the paper industry. With a clear understanding of the mechanism of starch particle reduction during extrusion, the extruded starch particle size can be tailored according to the different purposes of the final uses.

9.2 Recommendations for future work

9.2.1 Further improve the process of starch grafting on fiber surfaces

In this work, a new method of cellulose fiber modification via starch grafting was developed. Large amount of starch (up to 10% based on fibers) was successfully grafted onto fiber surfaces with a high grafting yield of 90%. As a result, significant improvements on water removal and paper strength properties were achieved, which can provide great benefits for the paper industry. However, the current process of starch grafting can be further improved in the following two aspects: reducing the temperature for starch crosslinking and further improving the yield of starch grafting. In this work, AZC was used as the crosslinker and coupling agent to graft starch onto fiber surfaces, a high temperature above 80°C is needed to accomplish the starch grafting process for a short time, which would require large amount of thermal energy in practical productions. Therefore, a new crosslinker which requires a lower reaction temperature to accomplish the grafting process with a higher starch grafting yield (close to 100%) is needed.

In addition, in order to have a good tolerance of high shear forces normally applied in practical productions, both the bonding strength of starch hydrogel with fiber and the strength of the starch hydrogel itself should be further improved.

9.2.2 Conduct starch grafting treatment on recycled fibers

Normally recycled fibers have less bonding capability compared to virgin pulp fibers, due to the hornification effect. It might be challengeable to graft starch on recycle fibers because the recycled fiber normally has less free hydroxyl groups on its surface. However, whether the starch grafting treatment is applicable for recycled fiber is mainly dependent on whether the paper strength can be significantly improved.

9.2.3 Develop paper tensile strength modeling based on the results of this work and page equation

Unlike conventional papers which contain less than 1% cationic starch, the papers made of grafted fibers would contain 5% or even more starches. Therefore, besides the fiber-fiber bonding, the contributions of the fiber-starch bonding and starch-starch bonding in aspects of bonding strength and bonding area should also be taken into account when modeling paper tensile strength.

9.2.4 Characterize the prepared starch nanoparticles and conduct applications in papermaking

- determine the swelling and solubility of starch nanoparticles in water;
- study the application of starch nanoparticles in papermaking as a dry strength additive;
- conduct surface sizing experiment by using starch nanoparticle suspensions, and compare its performance with that of traditional surface sizing starches.

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